

# **The Distribution of Higher n-Alkanes in Partially Frozen Middle Distillate Fuels**

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## 19. ABSTRACT (Continued)

The precipitate data presented some problems of interpretation since it was observed that the waxy crystal precipitate matrix entrapped significant amounts of liquid (filtrate). Since it was not possible to remove all the entrapped liquid from the precipitate, an indirect method was used to determine the composition of the liquid-free crystalline material ("solids"). This method required that the fraction (Z) of entrapped liquid in the precipitate be known. Z could be determined from the GC data. These selected tracer materials (*k*-compounds) had relatively low freezing points and did not crystallize out at the temperatures under study, and therefore showed no appreciable concentration change with temperature in the filtrate. Two other techniques were also used to test the *k*-compound method. The first, using dyes as "tracers," proved less satisfactory than the *k*-compound method. The other, using high-pressure liquid chromatography, validated the *k*-compound method.

The data on solids which were obtained by these methods demonstrated that the higher n-alkanes play the key role in fuel crystallization at low temperatures, concentrating as much as tenfold in the crystallized solids compared to the liquid. Also, it was clearly shown that the n-alkanes form the major part, up to at least 95% by weight in some fuels, of the solid crystals formed.

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# THE DISTRIBUTION OF HIGHER $n$ -ALKANES IN PARTIALLY FROZEN MIDDLE DISTILLATE FUELS

## 1. INTRODUCTION

One of the tasks of the United States Navy Mobility Fuels program at the Naval Research Laboratory is to determine the effect of composition on the freezing point of liquid fuels [1,2]. The combination of requirements for ship and jet aircraft fuels of a low freezing point (to permit cold temperature operations around the world) and a flash point minimum (to reduce the hazard of storage and transport of liquid fuels on board ship) can create a problem. This is because many components of a fuel that tend to lower the freezing point (small hydrocarbons of higher vapor pressure) will also reduce the flash point. Because of these restraints, it is not always practical to produce fuels meeting these requirements from available crudes, and this limits the amount of JP-5 which can be produced from a barrel of crude. With increased knowledge and understanding of the components that first crystallize out of a cold fuel, it may be possible to modify refining techniques to increase the yield of Navy liquid fuels per barrel of crude without compromising either the freezing point or the flash point.

This report deals with a study directed towards partially frozen fuels and the isolation and characterization of the "precipitate" (solid crystals plus entrapped liquid) which can cause aircraft fuel-tank holdup, filter plugging, and related jet aircraft engine problems at low temperature operations. The study was expanded to include marine diesel fuel (DFM) in order to verify the inference that the same type or class of compounds was the first to crystallize out from any liquid fuel upon freezing.

The importance of the saturated hydrocarbon fraction, particularly the higher normal alkanes, in raising the freezing points of hydrocarbon fuels had been suggested by Dimitroff et al. [3,4]; Petrovic and Vitorovic [5]; Solash et al. [2]; and others. It was hoped that a study of the composition of the precipitate isolated from partially frozen fuels would shed further light on this point.

## 2. EXPERIMENTAL

An apparatus constructed for the isolation of the partially frozen fuel precipitate is shown in Fig. 1. The design was based on the fractional crystallization device used by Pitzer and Scott [6] and is similar to that of Dimitroff et al. [3,4,7] at the U.S. Army Fuels and Lubricants Laboratory. It is referred to as a "Liquid-Solid Separator" (or LSS) as it was called by Dimitroff.

The LSS consists of four components, A, B, C, and D, which were attached by means of O-ring joints with clamps. The assembled LSS was immersed in a refrigerated-and-stirred methanol bath in a large Dewar flask and cooled to the desired temperature. A weighed sample of the fuel (about 8 grams) was introduced through the open stopcock J by a hypodermic syringe with a long needle. A slow stream of dried nitrogen flowing through the stopcock K (with stopcocks I and L closed) and bubbling up through the fritted glass disc H prevented any liquid from flowing down through the disc while crystallization was taking place. After crystallization occurred, stopcocks J and K were closed, and L and I opened to allow a slow stream of nitrogen under pressure (up to 15 psig) from L to force the liquid filtrate through the fritted glass disc into the preweighed filtrate cup D. Additional entrapped liquid was forced out of the solid by stirring and tamping the precipitate. To carry this out, dome B was removed and the gelatinous precipitate stirred and pressed with a glass rod with a flattened end. This rod was either kept in the apparatus during the entire freezing process or cooled in dry ice before insertion. In this way the precipitate was spread more evenly over the fritted glass disc, eliminating channels through which the nitrogen could pass. Attempts to compress the precipitate by the rod and thus force

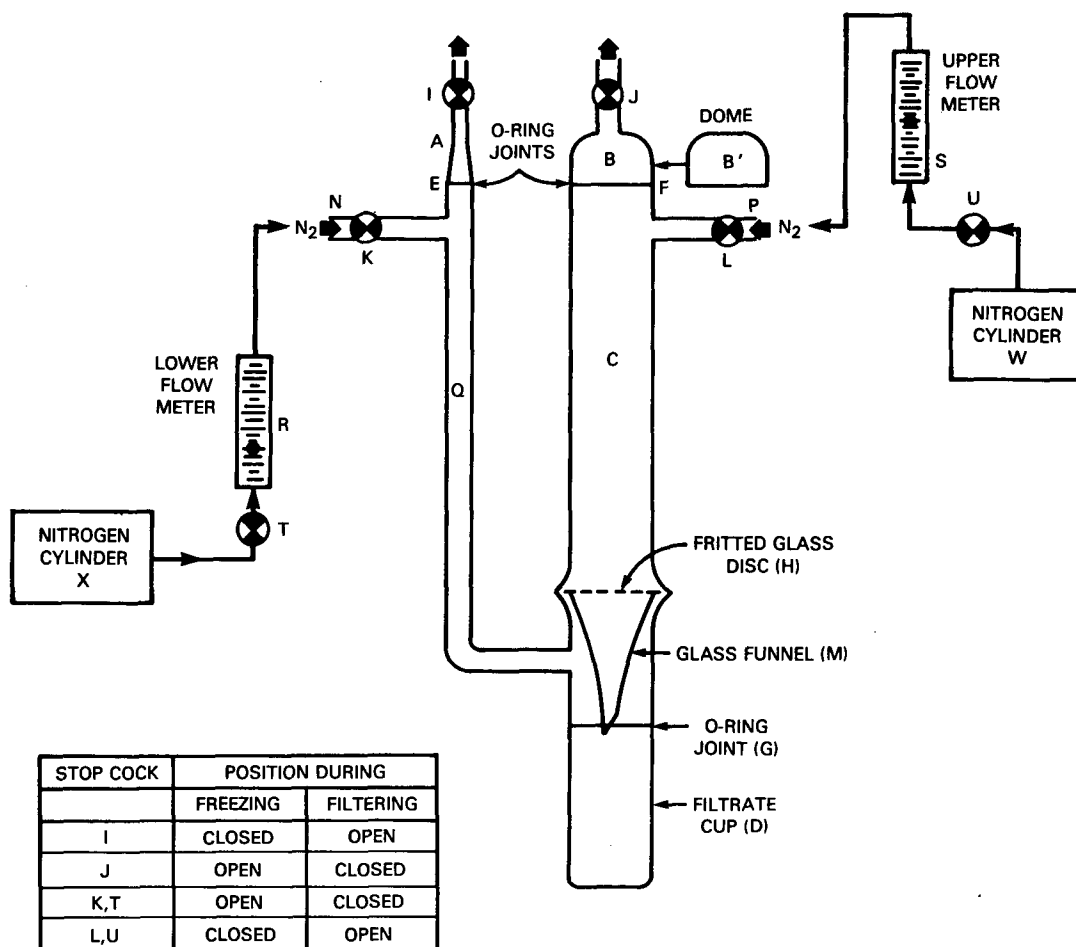


Fig. 1 — Liquid-solid separator

the liquid through the disc were unsuccessful. Dome B was replaced by a plain dome without a stopcock, B', and further filtering allowed to take place as before under nitrogen pressure. The plain dome eliminated nitrogen leaking through stopcock J. This process was repeated several times, especially with the DFM fuels, which proved quite difficult to separate. The data shown in some of the later tables were obtained by using this technique.

After the filtration, the filtrate was removed, weighed, and transferred to a sample bottle. The LSS was then allowed to warm to room temperature, and the melted crystals on the fritted disc H were forced by nitrogen under pressure to flow into a weighed flask. The residues on the disc and stirring rod were washed out with n-pentane and collected in a separate flask. After removing the pentane by bubbling nitrogen at ambient temperature and pressure through the solution, the residue was weighed and combined with the bulk precipitate in the flask. Careful tests showed that the higher n-alkanes (and other material) present in this residue were not swept out with the nitrogen sparging at a slow rate through the pentane solution. After thorough mixing, a sample was taken for analysis. Runs were made at several temperatures below the freezing point.

The concentrations of the n-alkanes in the original fuel samples, filtrates, and precipitates were determined using a 50-m, fused silica 0.2-mm i.d. capillary column in a Hewlett-Packard 5880 gas chromatograph (GC). The inlet split ratio was 60:1; the column oven was temperature-programmed from 50° to 200°C for the jet fuels and from 70° to 260°C for the diesel fuel; and the inlet and detector outlet temperatures were both 325°C. Iso-octane was used as an internal standard.

### 3. FUEL SAMPLES

Two different samples of JP-5 were used in this study. The first was a conventional petroleum-derived JP-5 (NRL No. 80-5). The other was a shale-derived fuel (NRL No. J-22) from the Shale-II refining process conducted by the Standard Oil Company of Ohio (SOHIO) at their refinery in Toledo, Ohio [8-10]. Both fuels met the military specification requirements for JP-5 jet turbine fuel [11]. The freezing points [12] of the petroleum and shale JP-5 fuels,  $-49^{\circ}$  and  $-48^{\circ}\text{C}$ , were below the specification maximum requirement [11] of  $-46^{\circ}\text{C}$ .

Because the emphasis of this study focused on n-alkane composition, many experiments were made with the shale sample since shale fuels usually have greater concentrations of n-alkanes and higher freezing points [2,9,10] than that of petroleum-derived fuels with a comparable distillation profile. As a result, data for J-22 fuel are reported for *only* five different temperatures; these data are average values obtained from as many as six runs at the same temperature. For the other three fuels, individual runs are reported in the data and results.

One of the samples of diesel fuel studied (NRL No. 82-8) was a conventional petroleum-derived DFM. The other (NRL No. 82-16) was a shale-derived fuel also from SOHIO's Shale-II refining process. The pour points of the fuels,  $-11^{\circ}$  and  $-23^{\circ}\text{C}$ , were well below the military specification maximum requirement [11] of  $-6.7^{\circ}\text{C}$ .

The freezing properties of all four fuels are listed in Table 1.

Table 1 — Freezing Properties of Middle Distillate Fuels

NRL Sample No.	JP-5		DFM	
	Shale II J-22	Petroleum 80-5	Shale II 82-16	Petroleum 82-8
Military Specifications (Max. $^{\circ}\text{C}$ )				
Freezing Point	-46	-46	—	—
Pour Point	—	—	-6.7	-6.7
Measured Properties ( $^{\circ}\text{C}$ )				
Freezing Point <sup>a</sup>	-48	-49 <sup>b</sup>	—	—
Pour Point <sup>c</sup>	—	—	-23	-11

<sup>a</sup> ASTM D2386

<sup>b</sup> From Inspection Report Data

<sup>c</sup> ASTM D97

### 4. RESULTS AND DISCUSSION

The GC chromatograms for all four fuels and the filtrates and precipitates associated with them are quite similar at first glance, but there are significant differences which affect the ease and quantitative accuracy of analysis. The chromatograms for the two JP-5 fuels are shown in Figs. 2 and 3, and those for the DFM fuels in Figs. 4 and 5.

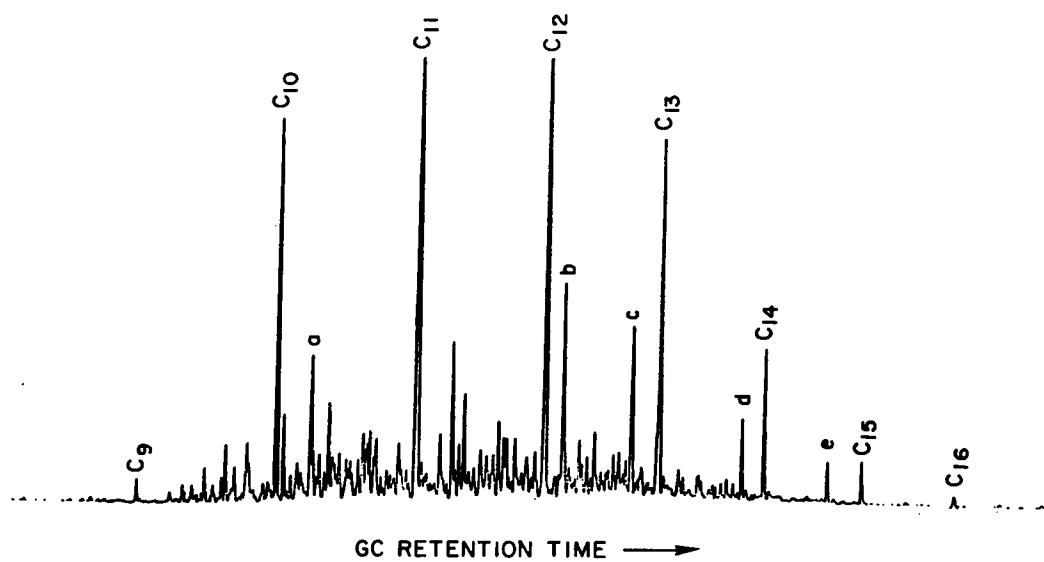


Fig. 2 — Fuel: J-22, JP-5 Shale II

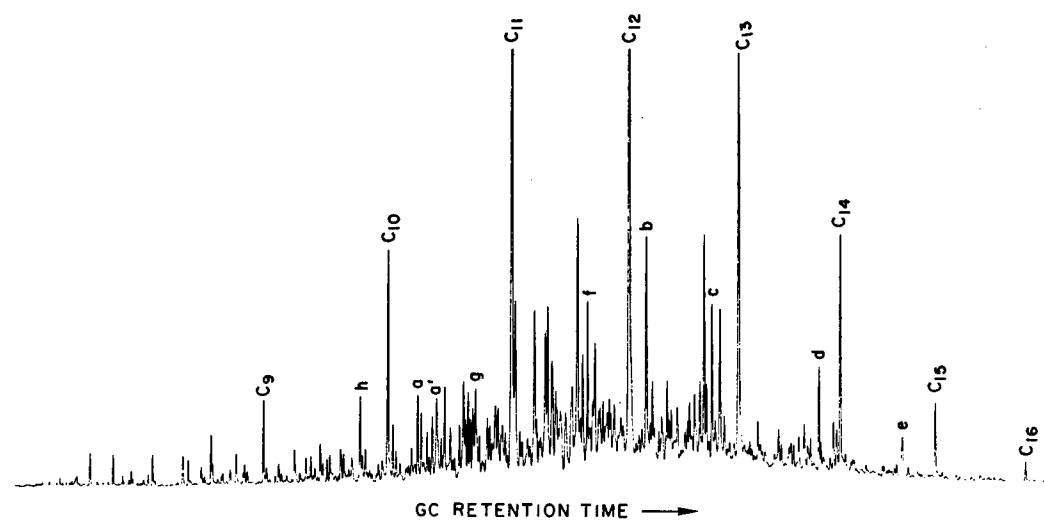


Fig. 3 — Fuel: 80-5, JP-5 Petroleum

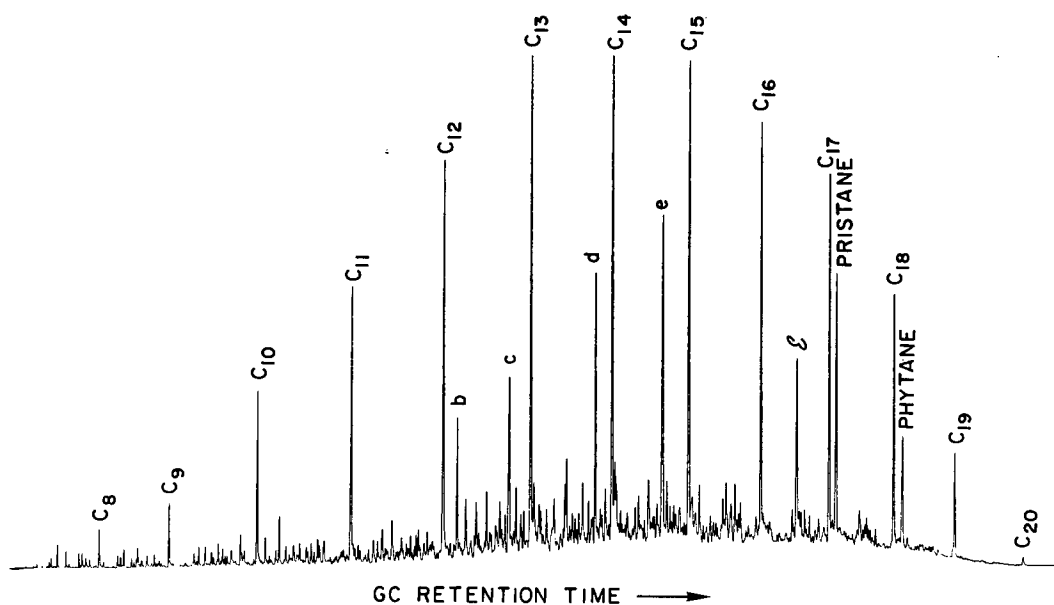


Fig. 4 — Fuel: 82-16, DFM Shale II

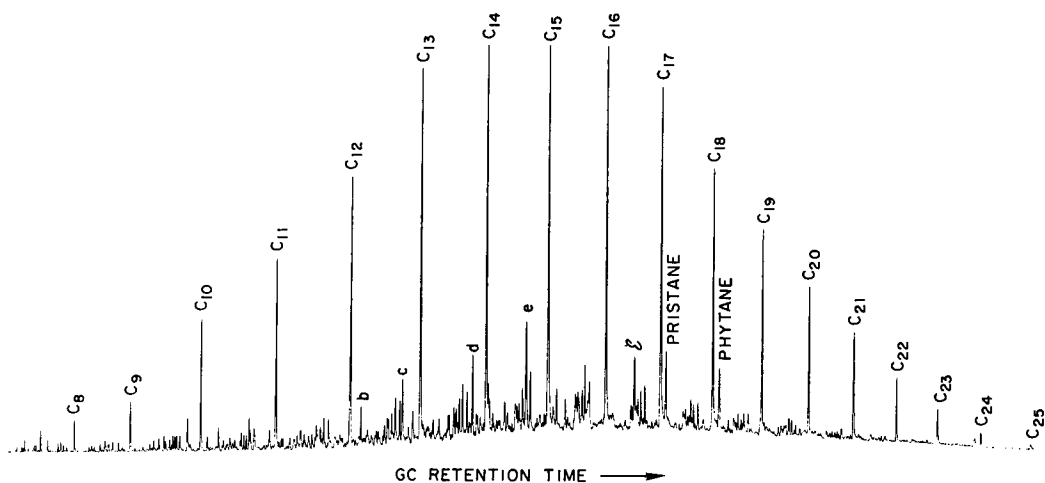


Fig. 5 — Fuel: 82-8, DFM Petroleum



The chromatograms for fuel J-22, a JP-5 derived from shale, is relatively simple. The components are bounded by normal nonane, n-C<sub>9</sub>, on the light end and by normal hexadecane, n-C<sub>16</sub>, on the heavy end, although these two components were present in concentrations too small to be measured accurately. The normal alkanes dominate the chromatogram, accounting for 26% by weight of the fuel (Table 2). There are a few other sharp, prominent peaks, some of which are labelled on the chromatogram for reasons discussed below. The baseline is relatively flat, and the quantitative analytical measurements seemed accurate and easily reproducible. Although there are a great many components in the fuel, the number of major peaks is relatively few compared with the other fuels.

Table 2 — n-Alkane Concentrations in Original Fuel Samples  
(X<sub>o</sub> = % w<sub>o</sub>/W<sub>o</sub>)

n-Alkane	JP-5		DFM	
	Shale II	Petroleum	Shale II	Petroleum
C <sub>8</sub>			0.07	0.07
C <sub>9</sub>			0.17	0.12
C <sub>10</sub>	4.50	1.01	0.53	0.40
C <sub>11</sub>	8.55	4.36	1.11	0.60
C <sub>12</sub>	7.10	5.35	1.61	1.00
C <sub>13</sub>	4.41	3.78	2.54	1.44
C <sub>14</sub>	1.36	1.67	2.91	1.88
C <sub>15</sub>	0.35	0.54	2.66	2.00
C <sub>16</sub>		0.15	2.30	1.89
C <sub>17</sub>			2.26	1.63
C <sub>18</sub>			1.60	1.22
C <sub>19</sub>			0.68	1.08
C <sub>20</sub>			0.06	0.71
C <sub>21</sub>				0.50
C <sub>22</sub>				0.30
C <sub>23</sub>				0.16
C <sub>24</sub>				0.07
<b>Total %</b>	<b>26.27</b>	<b>16.86</b>	<b>18.50</b>	<b>15.07</b>

The separation of the filtrate and precipitate fractions from J-22 was straightforward; it ended when no further liquid filtered through the fritted glass disc under nitrogen pressure. The precipitate fraction was not tamped down with the glass rod nor was the nitrogen pressure above 7 to 8 psi.

The chromatogram of fuel 80-5, a petroleum-derived JP-5, shows normal alkanes from n-C<sub>8</sub> to n-C<sub>17</sub> present in generally greater concentrations than other components although they account for less than 17% of the weight (Table 2). The baseline is not nearly as flat as that for J-22, and there are many more "shoulders" on the n-alkane peaks which did not all disappear by altering the GC program. Other prominent peaks, labelled by letters, are not as sharp and distinct, nor do they start and end on a straight baseline as do their counterparts in J-22. Considerably greater deviations in the quantitative analyses of the GC traces occurred with 80-5 compared to J-22. Therefore, multiple analyses were run through the GC to obtain reproducible results. The difficulty in separating the filtrate and precipitate fractions of this fuel led to modifying the separation technique by tamping and by increasing the nitrogen pressure.

Ease of analysis did not improve with the diesel fuels, the chromatograms of which are shown in Figs. 4 and 5; the concentrations are given in Table 2. Again the chromatogram for fuel 82-16, a

shale-derived DFM, is considerably simpler than that of the petroleum-derived DFM, 82-8. The difficulties encountered with the 80-5 fuel, mentioned above, were, however, present with these fuels to an even greater degree.

## Filtrate

The filtrate solubility data for the four fuels are plotted as the logarithm of n-alkane concentration in the filtrate (as weight percent) vs the reciprocal absolute temperature ( $1000/T, K$ ). For each of the four fuels, the data for all the n-alkanes form straight lines, as would be expected for a Van't Hoff solubility plot. All of the slopes were determined by a least squares fit of the actual data taken; the compositions at the freezing point were not included in the fit.

The six n-alkanes present in measurable quantities in the J-22 jet fuel are plotted in Fig. 6. The slope of the line for the lowest n-alkane, n-C<sub>10</sub>, has a slight positive value indicating a small increase in concentration with decreasing temperature. For the next n-alkane, n-C<sub>11</sub>, the data show a very small negative slope as the concentration in the filtrate decreases very slightly with the temperature. A slightly negative to slightly positive slope would be consistent for a component from which a very small, but increasing amount of crystals form with decreasing temperature. Because the concentration of n-C<sub>10</sub> and n-C<sub>11</sub> are relatively very high in J-22, the concentration of their crystals in the solid phase should be modest, but real, as it was indeed found to be. If the concentrations of n-C<sub>10</sub> and n-C<sub>11</sub> were not as high, then a negative slope of greater magnitude would be necessary before a measureable amount of crystals could be found in the solid phase. The data for the remaining n-alkanes show definite negative slopes which increase in magnitude with carbon number. The shaded points in Fig. 6 represent the original fuel concentrations for each alkane plotted at the freezing point ( $-48^{\circ}C$ ). Since this temperature (actually the melting point) is the point at which the last trace of solid material redissolves, the composition at this point should be the same as that of the liquid fuel. As expected, these concentrations fell close to the plotted lines in almost all cases. The normalized data in Table 3 for each n-alkane going from left to right approach unity at the freezing point of  $-48^{\circ}C$  which, of course, is predicted by the data in Fig. 6. The descending columns in Table 3 show decreasing concentrations as carbon number increases.

The five highest n-alkanes present in the petroleum-derived jet fuel 80-5 are shown in Fig. 7. For each of these n-alkanes, n-C<sub>12</sub> through n-C<sub>16</sub>, the plot shows a definite negative slope which increases in magnitude with the carbon number. The slopes of the curves for the two smallest n-alkanes, n-C<sub>10</sub> and n-C<sub>11</sub>, are perfectly flat, indicating a small amount of crystalline solid freezing out of the fuel. The data are listed in Table 4, but they are not plotted in Fig. 7, as they would overlap existing curves. Thus the data for fuels 80-5 and J-22 indicate that the normal alkanes behave in an identical manner when the fuels are partially frozen.

The two diesel fuels show a much wider spectrum of n-alkanes, from n-C<sub>8</sub> to n-C<sub>20</sub>, in the shale-derived 82-16, and from n-C<sub>8</sub> to n-C<sub>24</sub> in the petroleum-derived 82-8. The filtrate data for the five n-alkanes, n-C<sub>15</sub> through n-C<sub>19</sub>, are shown in Table 5 and plotted in Fig. 8. The slopes of the lines for these components are negative, with magnitude increasing with the carbon number. The concentrations of n-C<sub>20</sub> were too small to give accurate results. For the sake of clarity the data for the lower alkanes were not plotted in Fig. 8. The concentrations of these lighter n-alkanes in the fuel are low, and since few crystals if any would seem to be formed over the temperature range studied, it is unlikely that there would be any noticeable concentration of these components in the solid phase. It is clear, however, that the higher alkanes in the shale-derived DFM behave in exactly the same way as do the n-alkanes in both JP-5 fuels.

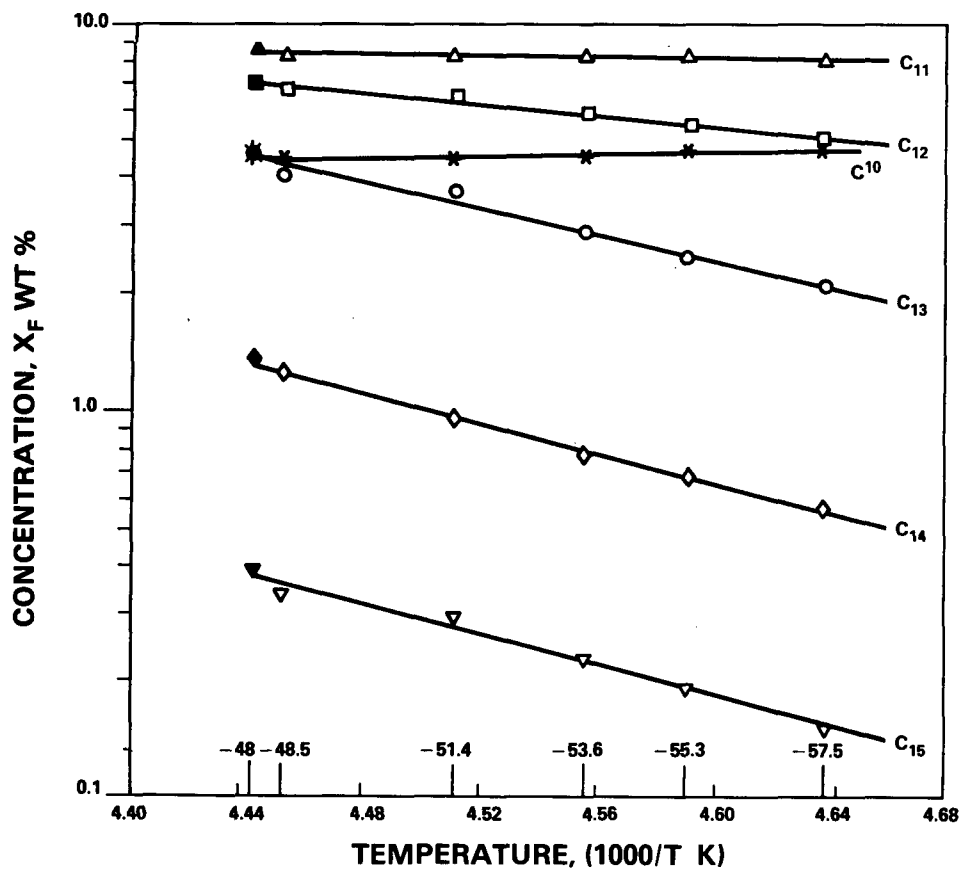


Fig. 6 — n-Alkanes in filtrate. Fuel: J-22, JP-5 Shale II.  
Solid symbols indicate concentration at freezing point.

Table 3 — n-Alkane Concentrations in Filtrate of Fuel J-22,  
JP-5 Shale II, as Function of Temperature

°C	Normalized Concentrations ( $X_F'$ ) *					
	-57.5	-55.3	-53.6	-51.4	-48.5	-48**
<u>n-Alkane</u>						
C <sub>10</sub>	1.04	1.03	1.01	1.00	0.98	0.97
C <sub>11</sub>	0.94	0.96	0.97	0.98	0.97	0.98
C <sub>12</sub>	0.71	0.77	0.83	0.91	0.95	0.99
C <sub>13</sub>	0.47	0.56	0.67	0.83	0.92	1.00
C <sub>14</sub>	0.42	0.51	0.57	0.70	0.91	0.94
C <sub>15</sub>	0.43	0.54	0.66	0.83	0.97	0.97

\*Normalized data—concentration divided by concentration in original sample

\*\*Data extrapolated to freezing point (-48°C)

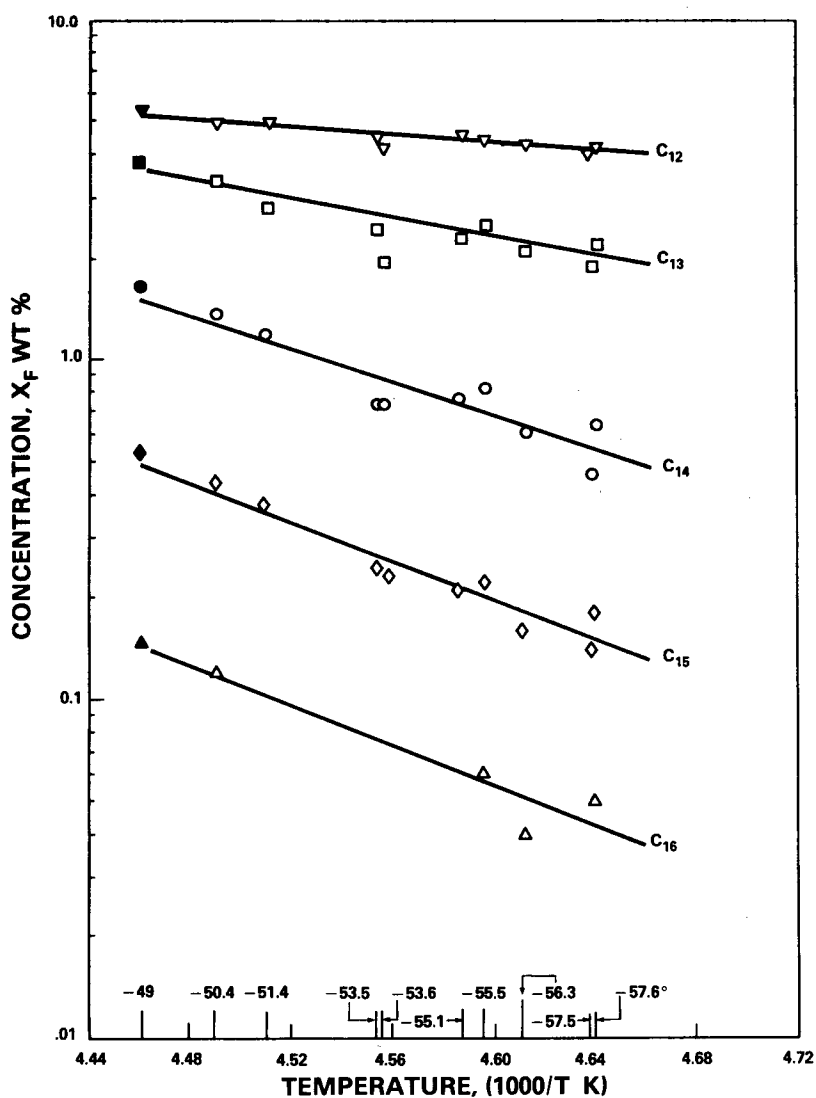


Fig. 7 — n-Alkanes in filtrate. Fuel: 80-5, JP-5 Petroleum.  
Solid symbols indicate concentration at freezing point.

Table 4 — n-Alkane Concentrations in Filtrate of Fuel 80-5, JP-5 Petroleum  
as Function of Temperature

°C	Normalized Concentrations ( $X_F'$ ) *									
	-57.6	-57.5	-56.3	-55.5	-55.1	-53.6	-53.5	-51.4	-50.4	-49**
<u>n-Alkane</u>										
C <sub>10</sub>	1.11	0.97	0.83	1.07	1.01	0.93	0.93	1.00	1.05	0.98
C <sub>11</sub>	0.97	0.92	1.00	0.95	0.97	0.89	0.90	1.00	0.96	0.95
C <sub>12</sub>	0.79	0.76	0.81	0.83	0.85	0.80	0.82	0.94	0.93	0.96
C <sub>13</sub>	0.59	0.50	0.57	0.67	0.62	0.52	0.65	0.74	0.89	0.84
C <sub>14</sub>	0.38	0.27	0.37	0.49	0.46	0.44	0.44	0.71	0.82	0.89
C <sub>15</sub>	0.34	0.26	0.29	0.41	0.38	0.42	0.44	0.67	0.80	0.90
C <sub>16</sub>	0.34	—	0.26	0.42	—	—	—	—	0.82	0.95

\*Normalized data—concentration divided by concentration in original sample

\*\*Data extrapolated to freezing point (-48°C)

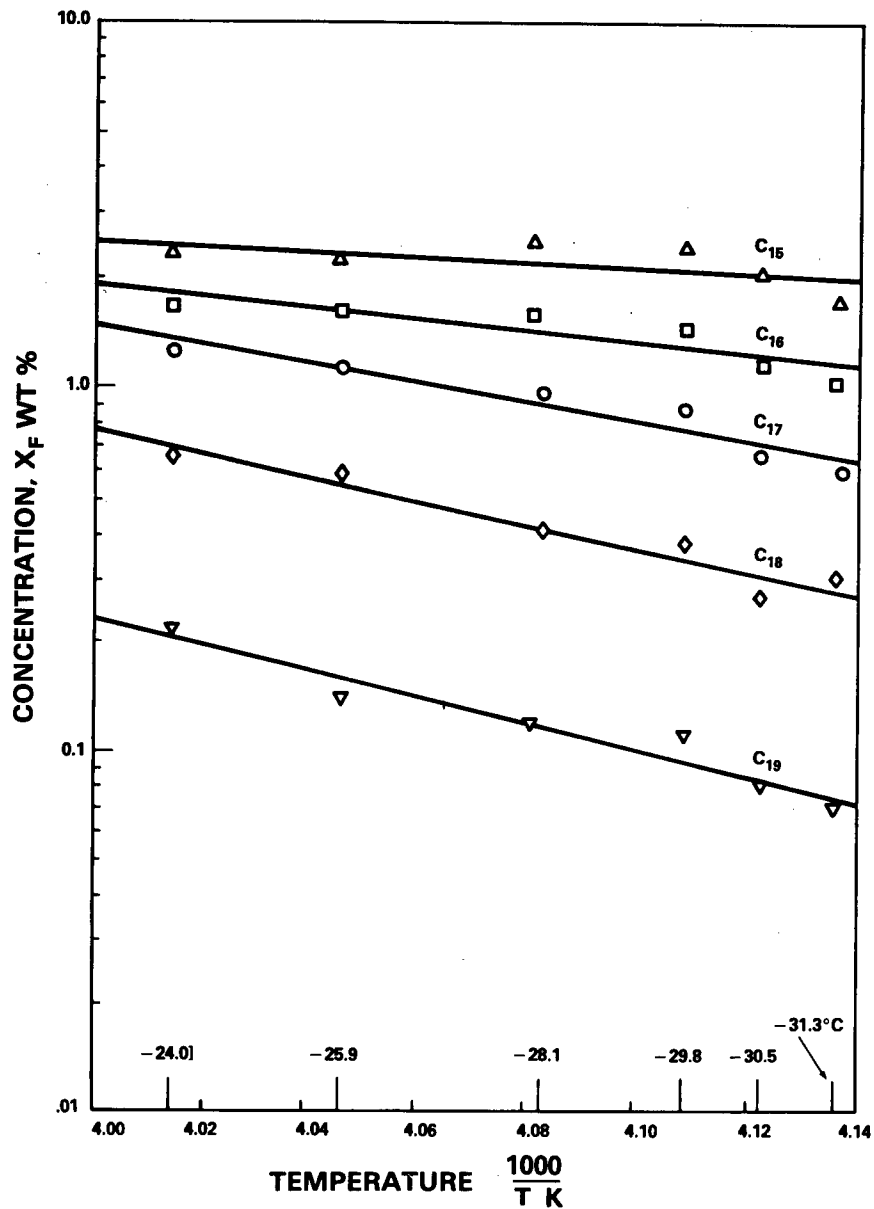


Fig. 8 — n-Alkanes in filtrate. Fuel: 82-16, DFM Shale II.

Table 5 — n-Alkane Concentrations in Filtrate of Fuel 82-16,  
DFM Shale II, as Function of Temperature

°C	Normalized Concentrations ( $X_F$ ) *					
	-31.3**	-30.5	-29.8	-28.1	-25.9	-24.0
<u>n-Alkane</u>						
C <sub>9</sub>	1.07	0.99	1.12	1.12	0.99	0.99
C <sub>10</sub>	1.17	0.98	1.13	1.11	0.98	0.98
C <sub>11</sub>	1.05	0.98	1.13	1.11	0.99	0.96
C <sub>12</sub>	1.05	0.98	1.13	1.12	0.99	0.96
C <sub>13</sub>	1.04	0.97	1.11	1.10	0.98	0.96
C <sub>14</sub>	1.00	0.93	1.09	1.09	0.98	0.94
C <sub>15</sub>	0.79	0.76	0.91	0.93	0.85	0.86
C <sub>16</sub>	0.54	0.50	0.63	0.69	0.70	0.73
C <sub>17</sub>	0.32	0.29	0.39	0.43	0.51	0.56
C <sub>18</sub>	0.23	0.17	0.23	0.27	0.37	0.42
C <sub>19</sub>	0.12	0.11	0.16	0.17	0.20	0.33

\*Normalized data—concentration divided by concentration in original sample

\*\*Run made six months after the others—data normalized against fuel analysis made at time of run

The behavior of the n-alkanes in fuel 82-8, a petroleum-derived DFM, is very similar to that in the other fuels. To preserve readability, only the filtrate data for the n-alkanes n-C<sub>18</sub> through n-C<sub>23</sub> appear in Fig. 9. The filtrate data for the two lowest n-alkanes, n-C<sub>8</sub> and n-C<sub>9</sub>, showed flat lines with no slope. The next six, n-C<sub>10</sub> through n-C<sub>15</sub>, show essentially the same, slightly negative slope. The negative slope increases with carbon number from n-C<sub>16</sub> through n-C<sub>21</sub>, the slope remaining fairly constant for the three heaviest n-alkanes. The concentrations, however, are very low for the three lightest and three heaviest n-alkanes, and great accuracy cannot be expected.

For all four fuels reported here, as well as for a petroleum-derived JP-5 fuel very low in n-alkanes reported elsewhere [13], the filtrate behavior of the heavier n-alkanes with decreasing temperature below the freezing point is very similar. The equilibrium between frozen n-alkane crystals in the solid phase and the concentration of n-alkane in the liquid phase is clearly identical to the solubility of crystals in a solute, with the liquid concentration data following a Van't Hoff solubility plot. It is difficult to determine whether the slight variations from one fuel to another, noted above, are significant, or due to the difficulty of obtaining easily reproducible results.

A careful study of the fuel and filtrate chromatograms was made for each of the four to discover other components of the fuel whose concentration in the filtrate was regularly lower than that in the fuel, as was the case with the heavier n-alkanes and would be for a component that crystallized out of solution to a reasonable extent. Not one could be found in any of the four fuels. Therefore a conclusion, indicated by a study of the filtrate data above, is that only the n-alkanes freeze or crystallize out of the fuel in the temperature ranges studied, which in each case was in the vicinity of the freezing point of that fuel. The filtrate data in the accompanying figures and tables all demonstrate the importance of the role of the higher n-alkanes in the freezing of jet and diesel fuels.

### Precipitate

The n-alkane concentrations in the precipitate are not presented in this report, although some have been reported elsewhere for J-22 jet fuel [14]. In the case of J-22 the separation of the liquid and

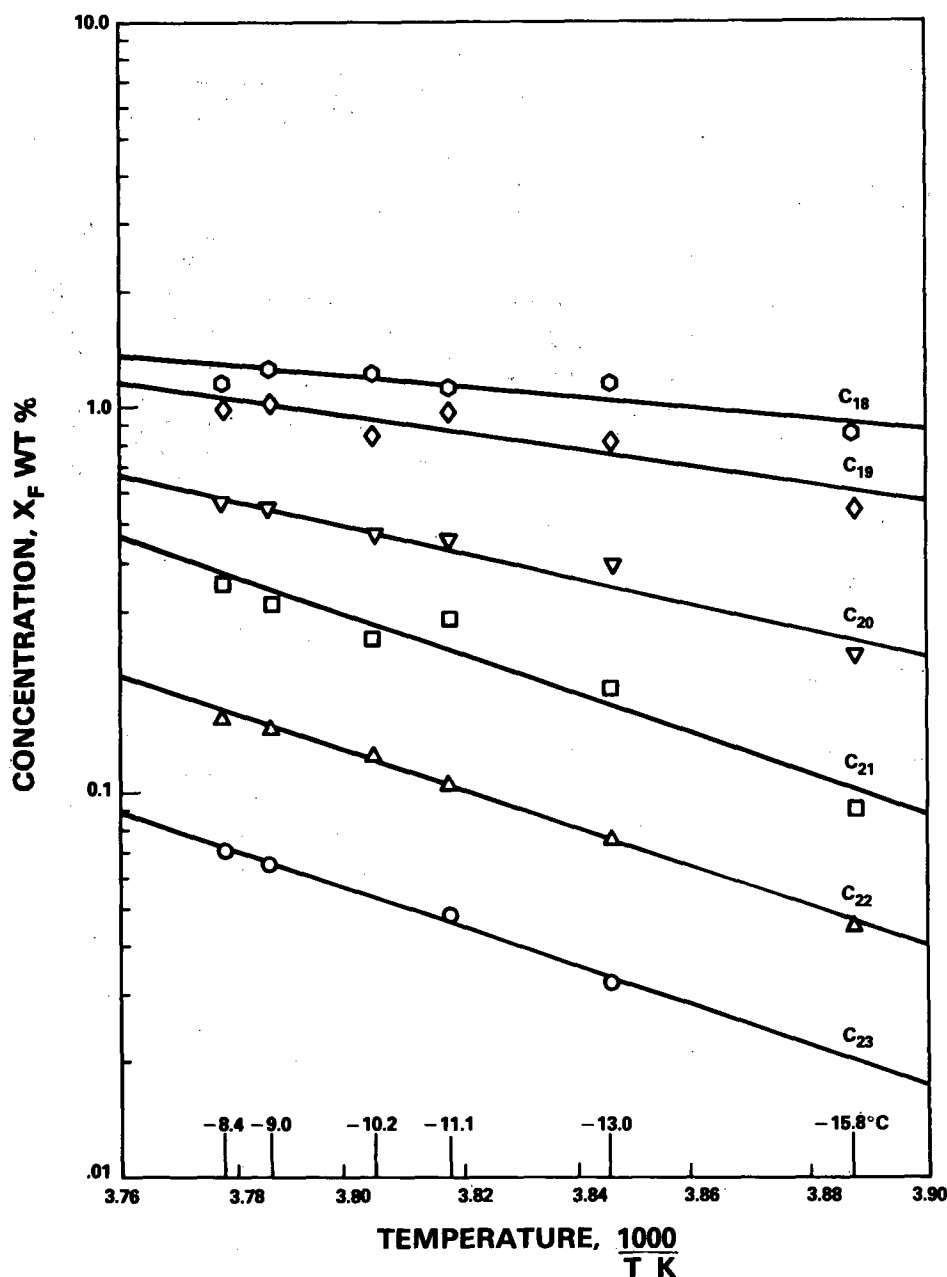


Fig. 9 — n-Alkanes in filtrate. Fuel: 82-8, DFM Petroleum.

precipitate fractions was relatively straightforward. The nitrogen pressure was maintained at a low value, and no tamping or stirring was necessary. As a result the amount of precipitate increased directly with decreasing temperature and a simple relationship was obtained between the filtrate and precipitate concentrations. But since it was observed that the waxy crystal matrix, of which the precipitate consisted, trapped significant amounts of filtrate, it was not the composition of the precipitate in which interest lay, but rather in the composition of the actual crystalline solids formed. In the three other fuels, 80-5, 82-16, and 82-8, the amount of liquid trapped in the crystalline matrix (i.e., in the precipitate) was relatively greater than that in the J-22, and it was necessary to introduce tamping and considerably higher nitrogen pressure to effect a satisfactory separation. Even then, however, the amount of trapped liquid was large, and only by indirect methods was it possible to estimate the amount of true solids present and the composition of those solids.

### Estimating Alkane Concentration in Solids Fraction of Precipitate

Since the precipitate contains some solid crystals and some entrapped liquid, let  $Z$  equal the weight fraction of liquid trapped in the precipitate:

$$W_L = ZW_P, \quad (1)$$

where  $W_L$  and  $W_P$  are the weights of liquid and precipitate. The mass balance in the precipitate may be expressed as

$$W_P = W_S + W_L, \quad (2)$$

where  $W_S$  is the weight of the solids in the precipitate. Substituting for  $W_L$  from Eq. (1) in Eq. (2), and solving for  $W_S$  we get

$$W_S = (1 - Z)W_P. \quad (3)$$

For a given solid component, A, (an alkane) its mass balance in the precipitate is

$$w_P = w_S + w_L, \quad (4)$$

where the lower case  $w$ 's are the weights of component A in the precipitate, solids, and liquid fractions. The concentrations of A in the solids, liquid, and precipitate ( $X_S$ ,  $X_L$ ,  $X_P$ ) are

$$X_S = w_S/W_S \quad (5)$$

$$X_L = w_L/W_L \quad (6)$$

$$X_P = w_P/W_P. \quad (7)$$

Solving Eqs. (5 to 7) for  $w_S$ ,  $w_L$ , and  $w_P$ , substituting in Eq. (4) we get

$$X_P W_P = X_S W_S + X_L W_L. \quad (8)$$

Substituting for  $W_L$  (Eq. (1)) and  $W_S$  (Eq. (3)) in Eq. (8), and solving for  $X_S$ , we obtain

$$X_S = (X_P - ZX_L)/(1 - Z). \quad (9)$$

Since the liquid portion of the precipitate is entrapped filtrate, the concentrate of A in the liquid is equivalent to that in the filtrate ( $X_F$ ). Substituting  $X_F$  for  $X_L$  in Eq. (9) we get

$$X_S = (X_P - ZX_F)/(1 - Z). \quad (10)$$

Equation (10) expresses the concentration of any component A in the solid fraction of the precipitate as a function of its concentration in the filtrate ( $X_F$ ) and precipitate ( $X_P$ ), and the fraction of liquid in the precipitate ( $Z$ ). We have determined  $X_F$  and  $X_P$ , and the problem is to estimate  $Z$ .

### Estimation of Z

If there is a species  $k$  in the precipitate which has a very low freezing point and does not freeze (form crystals) under the conditions of the experiment, it would therefore be present only in the *liquid* fraction of the precipitate. It is possible to estimate  $Z$  by making use of this information and applying Eq. (10). Solving Eq. (10) for  $Z$ , we obtain

$$Z = (X_P - X_S)/(X_F - X_S). \quad (11)$$

But if there is no  $k$  in the solids,  $X_S = 0$  for  $k$ , and Eq. (11) becomes

$$Z = X_P/X_F. \quad (12)$$

The  $Z$  obtained from Eq. (12) for component  $k$  is also applicable to the solid A components since it is the result of the same dilution of the precipitate by liquid filtrate. Hence, we can estimate  $Z$  by means of the ratio of component  $k$  in the precipitate to that of the filtrate.



### Estimating the Fraction of Solids in the Sample

From the weights of total material in the sample ( $W_0$ ), filtrate ( $W_F$ ), precipitate ( $W_P$ ), the fractions of filtrate (F), precipitate (P), and solids (S) can be estimated as follows: By definition

$$F = W_F/W_0 \quad (13)$$

$$P = W_P/W_0 \quad (14)$$

$$S = W_S/W_0 \quad (15)$$

Substituting for  $W_S$  (from Eq. (3)) and using  $W_P$  (from Eq. (14)) in Eq. (15), we get

$$S = (1 - Z)P \quad (16)$$

Thus, by means of Eqs. (13), (14), and (16), and knowing  $Z$ , we can calculate F, P, and S.

### Choice of Noncrystal-Forming Components for Estimating $Z$

After careful examination of the chromatograms for the jet fuel J-22, two  $k$  compounds were selected, labelled **a** and **b** in Fig. 3, which seem not to have formed solid crystals. The retention time of **a** was between that of  $C_{10}$  and  $C_{11}$ , and that of **b** between  $C_{12}$  and  $C_{13}$ . They were tentatively identified by GC-mass spectrometry as 4-methyl decane and 2-methyl dodecane. The melting point of 4-methyl decane is  $-92.9^\circ\text{C}$  [15], well below the temperatures of these experiments. The drastic difference in freeze point effected by branching ( $n-C_{11} = -25.6$ ) is typical of branched isomers vs straight-chain alkanes. These two compounds were selected because they exhibited sharp, distinct GC peaks, and because their concentrations in the filtrate and precipitate were essentially constant with temperature in both the filtrate and precipitate. The average normalized concentration data (relative to concentrations in the original sample) were slightly greater than unity (about 1.06) in the filtrate, and slightly below unity (about 0.91) in the precipitate. This would be expected for compounds which do not crystallize out, since their concentrations (relative to that in the sample) in the filtrate would rise as other materials precipitate out. Conversely, their concentrations in the precipitate (since they appear only in the liquid fraction of the precipitate) would decrease as the alkanes concentrate in the precipitate. Three other components labelled **c**, **d**, and **e** in Fig. 3 were also studied as possible  $k$  compounds, but they did not give consistent results.

It was hoped at first to be able to use the same two  $k$  compounds for the petroleum-derived jet fuel as for the J-22, but the difficulty of obtaining reproducible quantitative results from the GC traces forced us to modify the GC program temperatures and rates. As well as giving a straighter baseline and greater clarity and separation of the peaks, this change also resulted in doubling the residence time of the highest  $n$ -alkane. It seems to be a peculiarity of fuels analyzed by programmed gas chromatography that the traces of the same fuel may look quite different for different programs. Following a study of the traces for the 80-5 jet fuel, a whole set of possible  $k$  compounds, labelled by the letters **h**, **a**, **g**, **f**, **b**, **c**, and **d** in Fig. 3, were investigated. The same compounds identified in the J-22 GC trace have the same letter labels. Seven of these possible  $k$  compounds were used, since the majority always seemed to give very similar values of  $Z$ , with one or two (never the same ones) deviating substantially. Therefore the average value of  $Z$  obtained from these seven components was the value generally used in the calculations.

For the shale-derived DFM, fuel 82-16, the value of  $Z$  was obtained by taking the average value found by using as  $k$  compounds the components labelled **b**, **c**, **d**, **e**, and **f** in Fig. 4. They are rather widely scattered between  $n-C_{12}$  and  $n-C_{17}$ . The deviations among the values of  $Z$  found from these five compounds were very small in all cases. Note also that if the compounds pristane and phytane (identified in Fig. 4) together with the normal alkanes  $n-C_9$  through  $n-C_{12}$  were also used as  $k$  compounds, the overall average value of  $Z$  would be approximately the same as the value obtained from the five

components. Furthermore, only at the lowest temperatures was there any indication that some  $n\text{-C}_{13}$  crystals were formed.

Fuel 82-8, petroleum-derived DFM, turned out to be the easiest fuel for which to obtain a value of  $Z$ . The average values of  $Z$  found by taking as  $k$  compounds **b**, **c**, **d**, **e**, **e**,  $n\text{-C}_8$ ,  $n\text{-C}_9$ , and  $n\text{-C}_{10}$  were the same as the average values obtained by using all of the above compounds together with pristane, phytane, and the  $n$ -alkanes  $n\text{-C}_{11}$  through  $n\text{-C}_{14}$ . From these observations it is clear that none of them formed crystalline solids in the temperature range investigated;  $n\text{-C}_{15}$  was the lowest  $n$ -alkane to form any crystals, and this only at the lower temperatures. The data of Table 6 substantiate this conclusion. The  $Z$  values actually used were obtained as an average value of those obtained from taking all of the above mentioned components as  $k$  compounds. These components are well scattered throughout the lighter end of the GC trace and would all be expected to remain completely liquid at the given temperatures. It was surprising, nevertheless, to discover that all the  $Z$  values obtained from such a wide variety of components differed so little from each other.

Table 6 —  $n$ -Alkane Concentrations in Filtrate of Fuel 82-8, DFM Petroleum, as Function of Temperature

°C	Normalized Concentrations ( $X_F$ ) *					
	-15.8	-13.0	-11.1	-10.2	-9.0	-8.4
<u><math>n</math>-Alkane</u>						
$C_8$	1.01	1.00	1.00	0.97	1.03	1.10
$C_9$	1.07	1.04	1.07	1.04	1.07	1.14
$C_{10}$	1.07	1.07	1.12	1.04	1.11	1.18
$C_{11}$	0.97	1.09	1.04	1.02	1.02	1.09
$C_{12}$	0.97	0.97	1.09	0.98	1.05	0.99
$C_{13}$	0.96	0.99	1.05	1.00	1.03	1.07
$C_{14}$	1.04	1.06	1.10	1.03	1.03	1.17
$C_{15}$	0.96	1.04	1.07	1.02	1.05	1.04
$C_{16}$	0.94	1.03	1.08	0.96	1.09	1.06
$C_{17}$	0.83	1.00	1.04	0.98	1.07	1.03
$C_{18}$	0.68	0.93	0.91	0.99	1.04	0.94
$C_{19}$	0.50	0.75	0.79	0.78	0.95	0.91
$C_{20}$	0.32	0.55	0.64	0.66	0.77	0.80
$C_{21}$	0.18	0.37	0.57	0.51	0.63	0.70
$C_{22}$	0.15	0.25	0.35	0.41	0.49	0.53
$C_{23}$	—	0.20	0.30	—	0.41	0.44

\*Normalized data—concentration divided by concentration in original sample

### $n$ -Alkane Concentration in the Solids

By means of the concentrations of the various  $k$  components,  $Z$  values were calculated using Eq. (12). The average  $Z$  values were used to calculate the concentrations of each  $n$ -alkane in the solids using Eq. (10). The normalized concentrations are listed in Tables 7 to 10 for the four fuels studied at various temperatures.

All four fuels show the same characteristic behavior: the higher the  $n$ -alkane the greater is its concentration increase in the solid phase. The occasional aberrations in the highest  $n$ -alkane are most probably due to its low concentration in the raw fuel and the resultant difficulties of accurate quantitative analysis. The concentration of the lighter  $n$ -alkanes generally show an increase in concentration in

Table 7 — n-Alkane Concentrations in Solid Phase of Fuel J-22, JP-5 Shale II, as Function of Temperature

°C	Normalized Concentrations ( $X_S$ ) *				
	-57.5	-55.3	-53.6	-51.4	-48.5**
<u>n-Alkane</u>					
C <sub>10</sub>	0.42	0.44	0.33	0.31	0.08
C <sub>11</sub>	1.61	1.49	1.46	1.16	0.29
C <sub>12</sub>	4.26	3.90	4.42	3.68	0.96
C <sub>13</sub>	6.55	5.76	7.53	6.64	1.91
C <sub>14</sub>	8.01	7.57	9.85	9.48	2.76
C <sub>15</sub>	8.63	8.00	10.29	9.74	2.66

\*Normalized data—concentration divided by concentration in original sample

\*\*Data listed here because they are useful later on. The value of Z at this temperature was very inaccurate.

Table 8 — n-Alkane Concentrations in Solid Phase of Fuel 80-5, JP-5 Petroleum as Function of Temperature

°C	Normalized Concentrations ( $X_S$ ) *								
	-57.6	-57.5	-56.3	-55.5	-55.1	-53.6	-53.5	-51.4	-50.4
<u>n-Alkane</u>									
C <sub>10</sub>	0.32	0.26	0.04	0.16	0.14	0.10	—	0.17	—
C <sub>11</sub>	1.11	1.13	1.04	1.07	0.72	0.67	0.69	0.61	0.73
C <sub>12</sub>	3.76	3.54	3.82	3.86	2.64	2.89	3.19	2.31	3.30
C <sub>13</sub>	6.89	7.06	6.90	7.92	5.57	6.30	7.60	5.48	8.59
C <sub>14</sub>	9.99	10.11	10.50	12.16	8.46	9.14	12.50	8.82	15.72
C <sub>15</sub>	11.79	11.79	10.72	15.01	10.35	11.51	15.35	11.34	21.46
C <sub>16</sub>	11.49	11.76	10.88	14.86	10.88	14.26	15.88	14.09	20.54

\*Normalized data—concentration divided by concentration in original sample

Table 9 — n-Alkane Concentrations in Solid Phase of Fuel 82-16, DFM Shale II, as Function of Temperature

°C	Normalized Concentrations ( $X_S$ ) *					
	-31.3	-30.5	-29.8	-28.1	-25.9	-24.0
<u>n-Alkane</u>						
C <sub>14</sub>	0.94	0.82	0.76	0.73	0.44	0.50
C <sub>15</sub>	3.22	3.19	3.56	3.00	2.48	2.32
C <sub>16</sub>	6.91	7.57	7.52	7.41	6.24	6.32
C <sub>17</sub>	10.09	10.76	12.21	11.29	10.22	11.05
C <sub>18</sub>	11.38	12.46	14.34	13.79	12.93	14.73
C <sub>19</sub>	12.13	13.33	15.32	15.30	14.57	16.98
C <sub>20</sub>	14.44	15.44	18.42	19.65	15.96	21.58

\*Normalized data—concentration divided by concentration in original sample

Table 10 — n-Alkane Concentrations in Solid Phase of Fuel 82-8, DFM Petroleum, as Function of Temperature

°C	Normalized Concentrations ( $X_S'$ ) *					
	-15.8	-13.0	-11.1	-10.2	-9.0	-8.4
<u>n-Alkane</u>						
C <sub>15</sub>	0.08	0.14	—	0.01	0.35	0.12
C <sub>16</sub>	0.77	0.49	0.34	0.18	0.36	0.31
C <sub>17</sub>	2.74	1.44	1.39	0.93	1.01	0.88
C <sub>18</sub>	6.91	4.12	4.77	2.84	3.34	3.36
C <sub>19</sub>	10.18	7.05	8.09	5.69	6.96	6.54
C <sub>20</sub>	15.65	13.25	17.54	12.85	14.87	16.17
C <sub>21</sub>	18.62	17.16	23.30	19.04	22.70	25.70
C <sub>22</sub>	21.80	20.50	31.30	24.80	29.80	36.00
C <sub>23</sub>	24.10	22.80	36.30	30.20	34.80	44.10
C <sub>24</sub>	27.10	23.70	40.90	31.30	40.10	50.40

\*Normalized concentration—concentration divided by concentration in original sample

the solids as the temperature decreases. This is also expected as more crystals freeze out of the liquid and form part of the solid phase. On the other hand, it can be seen that the reverse is true of the heavier n-alkanes in the solid phase. At the higher temperatures they will form most of the solid crystalline phase. As the temperature decreases and more of the lighter n-alkanes appear in the solid phase, the absolute proportion of the heavier n-alkanes must get smaller, and so the concentration decreases with decreasing temperature. The data for J-22 at  $-48.5^\circ\text{C}$  listed in Table 8 should not be considered in this respect, as the value obtained for Z was obviously incorrect by a large factor. The concentration data in the filtrate and precipitate at this temperature seem consistent with other data, however, and so all are reported (cf. Fig. 6 and Table 3; also Fig. 8 and Table 15).

The values of the normalized n-alkane concentrations in the solid phase,  $X_S'$ , were calculated by dividing the values of  $X_S$  obtained from Eq. (10) by the concentration in the fuel,  $X_0$ , for each n-alkane. These are the values reported in Tables 7-10. The sensitivity of  $X_S'$  to the accuracy of the value of Z can be readily seen: an error of 5% in the value of Z when  $Z = 0.85$  causes an error of 25% in the value of  $X_S'$ , whereas an error of 5% in Z when  $Z = 0.70$  causes an error of 11% in  $X_S'$ . Thus one of the most important and difficult tasks was obtaining accurate values of Z. In general, however, the values of  $X_S'$  as a function of temperature show the expected relationship for a component freezing or crystallizing out of a liquid solution.

### Total Material Balance

By means of Eqs. (13), (14), and (16), the total material balances for the test runs were estimated. Tables 11-14 list the results for all four fuels. The percent recovery, defined as 100 times the ratio of the weight of filtrate plus precipitate to the weight of fuel, generally exceeded 99%, and only once fell below 98%. There was always some loss of fuel in the transfer from the syringe to the LSS, due in part to fuel remaining in the long needle, and so the recovery never reached 100%. Also there was some evaporation loss when the pentane solvent was removed by nitrogen bubbling.

The percent of crystalline solids S is shown in Fig. 10 as a function of temperature for the four fuels. The increase in the amount of solids with decreasing temperature is more pronounced for the jet fuels than for the DFM fuels. The slopes of the two lines for the DFM fuels are essentially equal, calculated by a least squares fit. This seems reasonable as the total n-alkane concentrations are not very different. The increase in S with decreasing temperature is greater for J-22, the shale-derived JP-5,

Table 11 — Total Material Balances—Fuel: J-22, JP-5 Shale II

°C	−57.5	−55.3	−53.6	−51.4	−48.5**
% Filtrate	44.7	67.8	79.6	90.1	83.9
% Precipitate	54.9	31.4	19.9	8.7	16.1
% Recovery	99.7	99.2	99.5	98.8	—
% Solids***	8.2	7.3	4.5	2.9	2.7
Z*	0.85	0.76	0.77	0.67	0.83

\*Fraction liquid (filtrate) in precipitate, P

\*\* Not accurate—some information lacking in these early runs

\*\*\*Freezing point extrapolated for S = 0 is −48°C

Table 12 — Total Material Balances—Fuel: 80-5, JP-5 Petroleum

°C	−57.6	−57.5	−56.3	−55.5	−55.1	−53.6	−53.5	−51.4	−50.4
% Filtrate	73.8	79.4	73.2	82.7	81.2	76.5	84.9	88.1	91.5
% Precipitate	24.0	20.2	26.3	16.7	18.1	23.4	14.5	11.6	8.0
% Recovery	97.7	99.6	99.5	99.5	99.3	99.9	99.5	99.6	99.5
% Solids**	6.0	6.1	5.3	4.2	5.7	4.0	3.2	2.7	1.1
Z*	0.75	0.7	0.80	0.75	0.69	0.83	0.78	0.77	0.86

\*Fraction liquid (filtrate) in precipitate, P

\*\*Freezing point extrapolated for S = 0 is −48.0°C

Table 13 — Total Material Balances—Fuel: 82-16, DFM Shale II

°C	−31.3	−30.5	−29.8	−28.1	−25.9	−24.0
% Filtrate	78.1	78.3	73.6	79.8	78.8	86.8
% Precipitate	20.9	21.0	25.0	19.6	20.9	12.9
% Recovery	99.0	99.3	98.6	99.4	99.8	99.7
% Solids**	6.9	5.9	5.8	5.5	4.6	3.6
Z*	0.68	0.72	0.77	0.72	0.78	0.72

\*Fraction liquid (filtrate) in precipitate, P

\*\*Freezing point extrapolated for S = 0 is −14.5°C

Table 14 — Total Material Balances—Fuel: 82-8 DFM, Petroleum

°C	-15.8	-13.0	-11.1	-10.2	-9.0	-8.4
% Filtrate	84.0	84.0	87.0	83.3	86.0	91.8
% Precipitate	15.4	15.0	11.7	16.0	12.3	7.8
% Recovery	99.3	99.1	98.6	99.3	98.3	99.6
% Solids**	4.2	4.2	2.6	2.7	1.9	1.5
Z*	0.73	0.72	0.78	0.83	0.84	0.81

\*Fraction liquid (filtrate) in precipitate, P

\*\*Freezing point extrapolated for S = 0 is -3.9°C

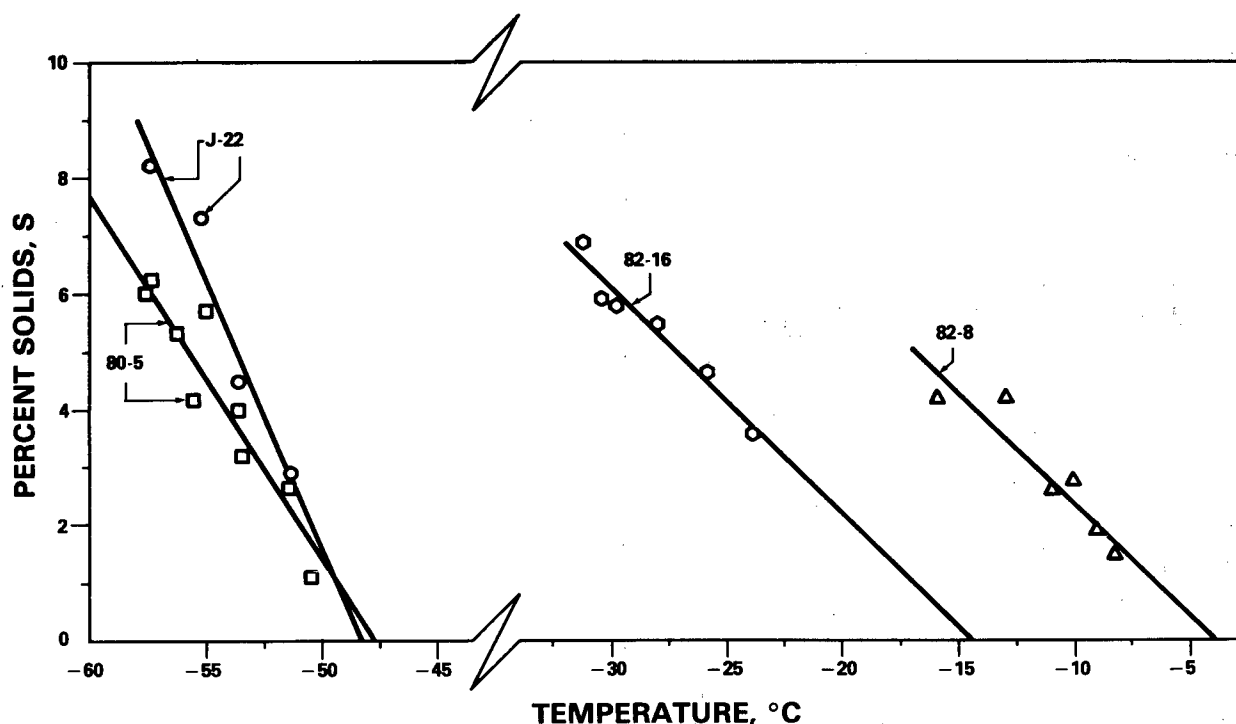


Fig. 10 — Percent solids as a function of temperature—all four fuels

than for 80-5, the petroleum-derived JP-5. This is to be expected since the total n-alkane concentration of J-22 is considerably greater than that of the 80-5 fuel. The scatter of the data for the two petroleum-derived fuels is greater than that of the Shale-II-derived fuels, probably indicative of the more complex composition of the petroleum-derived fuels (cf. Figs. 2 to 5).

The precipitate fraction in the case of J-22, where no tamping was used to assist the separation process, increased in a regular manner from 9% at -51.4°C to 54% at -57.5°C. The values of Z, the fraction of liquid in the precipitate, increased from 0.67 to 0.85 over the same temperature range. (The error in the data at -48.5°C has been mentioned above.) The high values of Z at the lower temperatures, with the concomitant uncertainties in the corresponding values of  $X_S'$ , show that tamping should have been introduced while investigating the behavior of the J-22 fuel. The values of S,  $X_S$ , and  $X_S'$ , all depend on the factor  $(1 - Z)$ , the uncertainty of which increases as Z approaches unity.

Due to the introduction of the tamping technique, the precipitate fractions for the 80-5 fuel were kept below 25%. This in turn kept the values of  $Z$  at a satisfactory value ( $<0.80$ ) for most of the experimental runs.

The most consistent values of  $Z$  were obtained for fuel 82-16, the shale-derived DFM. The values for  $S$  correlated well, but it did not follow that the filtrate data were also more self-consistent. There seem to be too many sources of inaccuracy for any one piece of data to be of major importance.

Fuel 82-8, petroleum-derived DFM, was the most difficult to separate into the filtrate and precipitate fractions. Nevertheless, the amount of precipitate was kept quite low, never exceeding 16% by weight even at  $5^{\circ}\text{C}$  below the pour point. The values of  $Z$  were higher in many cases ( $>0.80$ ) than the value required for good accuracy. Nevertheless, the trends were clearly defined in all cases.

### Percent of n-Alkanes in Fuel Found in the Solid Phase

Not only is the concentration of each n-alkane in the crystalline solid of interest, but of even greater interest is the percent of each n-alkane present in the fuel that is found in the solid phase. If we define  $X_S''$  as the percent of a given n-alkane present in the fuel that is found in the solid phase, then

$$X_S'' = (X_S'/X_0)S = X_S'S. \quad (17)$$

Based on Eqs. (10), (16), and (17), then

$$X_S'' = \frac{X_P - ZX_F}{(1 - Z)} \cdot \frac{1}{X_0} \cdot P(1 - Z) = P(X_P - Z \cdot X_F)/X_0. \quad (18)$$

Thus  $X_S''$  depends on directly determined experimental data and on the value of  $Z$ , which can only be determined indirectly.

Tables 15-18 give the variation of  $X_S''$  with the temperature for the four fuels investigated. These data are plotted for the higher n-alkanes in the four fuels in Figs. 11-14. The solid lines drawn in the figures were all calculated by linear regression, or least squares fit. As would be expected, the rate of increase in the percent in the solids increases with the carbon number.

Table 15 — Percent of Total Fuel n-Alkanes Found  
in Solid Phase as a Function of Temperature.  
Fuel: J-22, JP-5 Shale II.

$^{\circ}\text{C}$	Percent of Total Fuel n-Alkanes: $X_S'' = X_S' \cdot S$				
	-57.5	-55.3	-53.6	-51.4	-48.5
<u>n-Alkane</u>					
$\text{C}_{10}$	3.4	3.2	1.5	0.90	0.22
$\text{C}_{11}$	13.2	10.9	6.6	3.4	0.78
$\text{C}_{12}$	34.9	28.5	19.9	10.7	2.6
$\text{C}_{13}$	53.7	42.0	33.9	19.3	5.2
$\text{C}_{14}$	65.7	55.3	44.3	27.5	7.4
$\text{C}_{15}$	70.8	58.4	46.3	28.2	7.2

Freezing point extrapolated for  $X_S'' = 0$ : range  $-48.7^{\circ}$  to  $-47.2^{\circ}\text{C}$   
(average  $-47.9^{\circ}\text{C}$ )

Table 16 — Percent of Total Fuel n-Alkanes Found in Solid Phase  
as a Function of Temperature. Fuel: 80-5, JP-5 Petroleum.

°C	Percent of Total Fuel Alkanes: $X_S'' = X_S' \cdot S$								
	-57.6	-57.5	-56.3	-55.5	-55.1	-53.6	-53.5	-51.4	-50.4
<u>n-Alkane</u>									
C <sub>10</sub> *	1.9	1.6	0.2	0.7	0.8	0.4	—	0.5	0.0
C <sub>11</sub>	6.7	6.9	5.5	4.5	4.1	2.7	2.2	1.6	0.8
C <sub>12</sub>	22.6	21.6	20.3	16.2	15.0	11.6	10.2	6.2	3.6
C <sub>13</sub>	41.3	43.1	36.6	33.3	31.8	25.2	24.3	14.8	9.4
C <sub>14</sub>	59.9	61.7	55.8	51.1	48.2	36.6	40.0	23.8	17.3
C <sub>15</sub>	70.7	71.9	56.9*	63.0	59.0	46.0	49.1	30.6	23.6
C <sub>16</sub> *	68.9	71.7	57.8	62.4	62.0	57.0	50.8	38.0	22.6

\*Not plotted in Fig. 7

Freezing point extrapolated for  $X_S'' = 0$ : range: -51.4° to -45.4°C (average = -48.3°C)

Table 17 — Percent of Total Fuel n-Alkanes Found in Solid Phase  
as a Function of Temperature. Fuel: 82-16, DFM Shale II.

°C	Percent of Total Fuel n-Alkanes: $X_S'' = X_S' \cdot S$					
	-31.3	-30.5	-29.8	-28.1	-25.9	-24.0
<u>n-Alkane</u>						
C <sub>9</sub> - C <sub>13</sub>	0.0	0.0	0.0	0.0	0.0	0.0
C <sub>14</sub>	6.4	4.8	4.4	4.0	2.0	1.8
C <sub>15</sub>	22.1	18.9	20.6	16.5	11.4	8.4
C <sub>16</sub>	47.5	44.7	43.5	40.7	28.8	22.8
C <sub>17</sub>	69.3	63.6	70.6	62.0	47.2	39.9
C <sub>18</sub>	78.2*	82.8	82.9	75.7	59.7	53.2
C <sub>19</sub>	83.4*	88.7	88.5	84.0	67.3	61.3
C <sub>20</sub> *	99.2	91.2	106.5	107.9	73.8	77.9

\*Not plotted in Fig. 8

Freezing point extrapolated for  $X_S'' = 0$ : range: -21.6° to -10.8°C  
(average = -16.1°C)

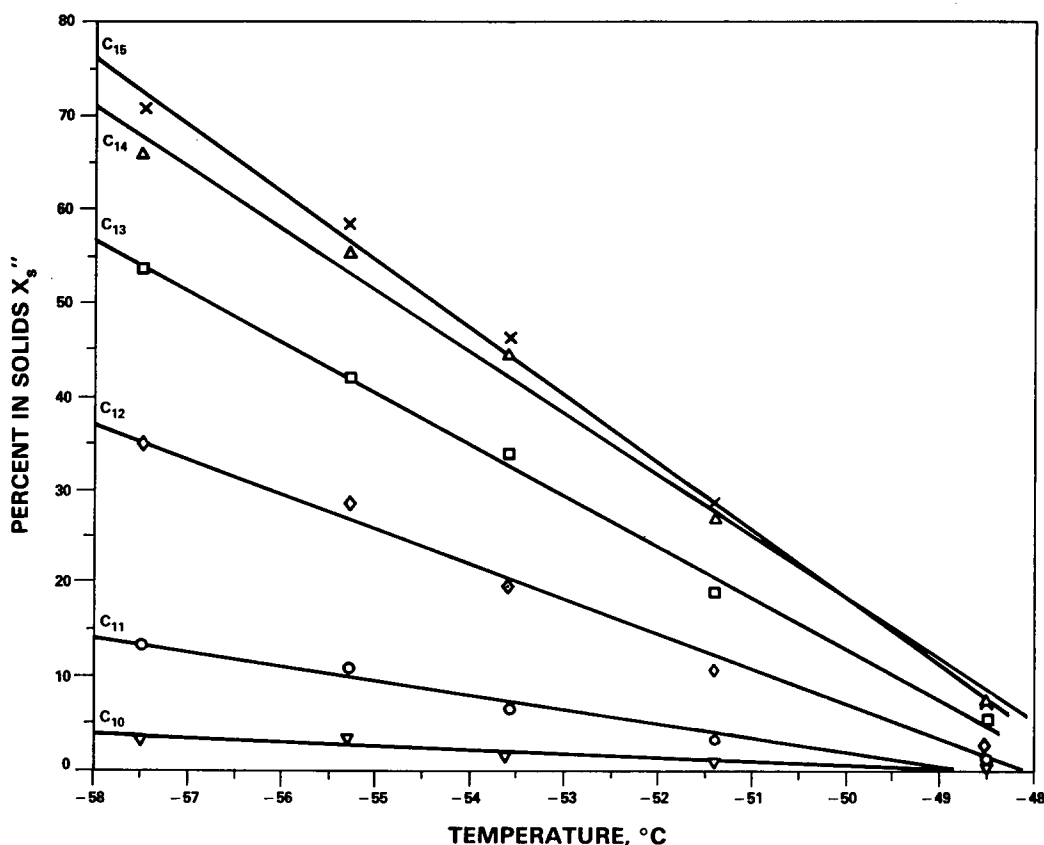


Table 18 — Percent of Total Fuel n-Alkanes Found in Solid Phase as a Function of Temperature. Fuel: 82-8, DFM Petroleum.

°C	Percent of Total Fuel n-Alkanes: $X_s'' = X_s' \cdot S$					
	-15.8	-13.0	-11.1	-10.2	-9.0	-8.4
<u>n-Alkane</u>						
$C_{13} - C_{14}^*$	—	—	—	—	—	—
$C_{15}^{**}$	0.4	0.6	—	0.03	0.7	0.2
$C_{16}^{**}$	3.2	2.1	0.9	0.5	0.7	0.5
$C_{17}^{**}$	11.4	6.1	3.6	2.5	2.0	1.3
$C_{18}$	28.7	17.5	12.4	7.8	6.5	5.1
$C_{19}$	42.3	29.9	21.1	15.6	13.5	9.9
$C_{20}$	65.1	56.3	45.8	35.2	28.9	24.4
$C_{21}$	77.5	72.9	60.7	52.2	44.0	38.7
$C_{22}$	90.8	87.1	81.3	67.9	57.8	54.4
$C_{23}$	100.1	97.0	94.8	82.9	67.4	66.6
$C_{24}^{**}$	112.9	100.8	106.6	85.7	77.9	76.1

\*Negligible, not plotted in Fig. 9

\*\*Not plotted in Fig. 9

Freezing point extrapolated for  $X_s'' = 0$ : range:  $-7.9^\circ$  to  $-1.2^\circ\text{C}$  (average =  $-4.6^\circ\text{C}$ )Fig. 11 — Percent of total fuel n-alkanes found in solid phase.  
Fuel: J-22, JP-5 Shale II.

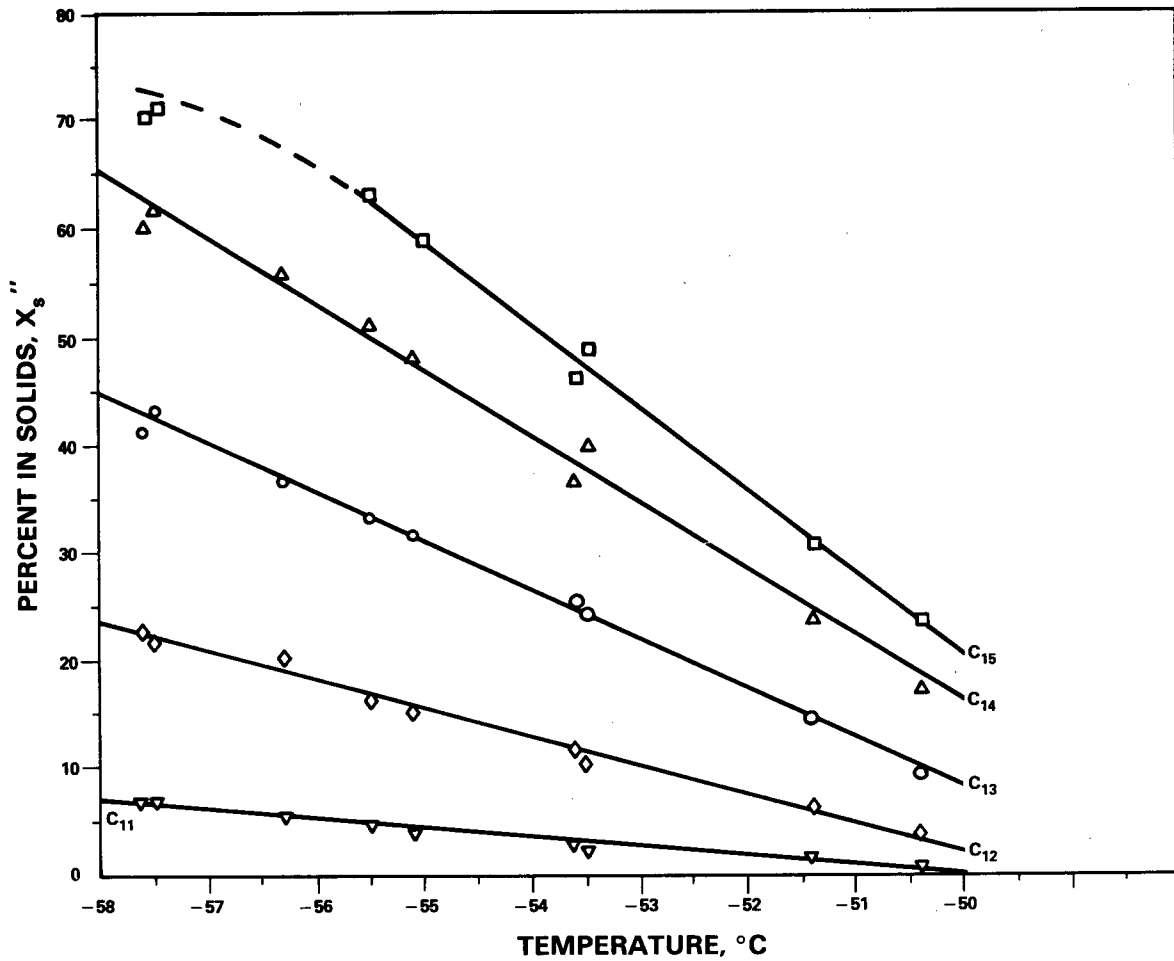


Fig. 12 — Percent of total fuel n-Alkanes found in solid phase.  
Fuel: 80-5, JP-5 Petroleum.

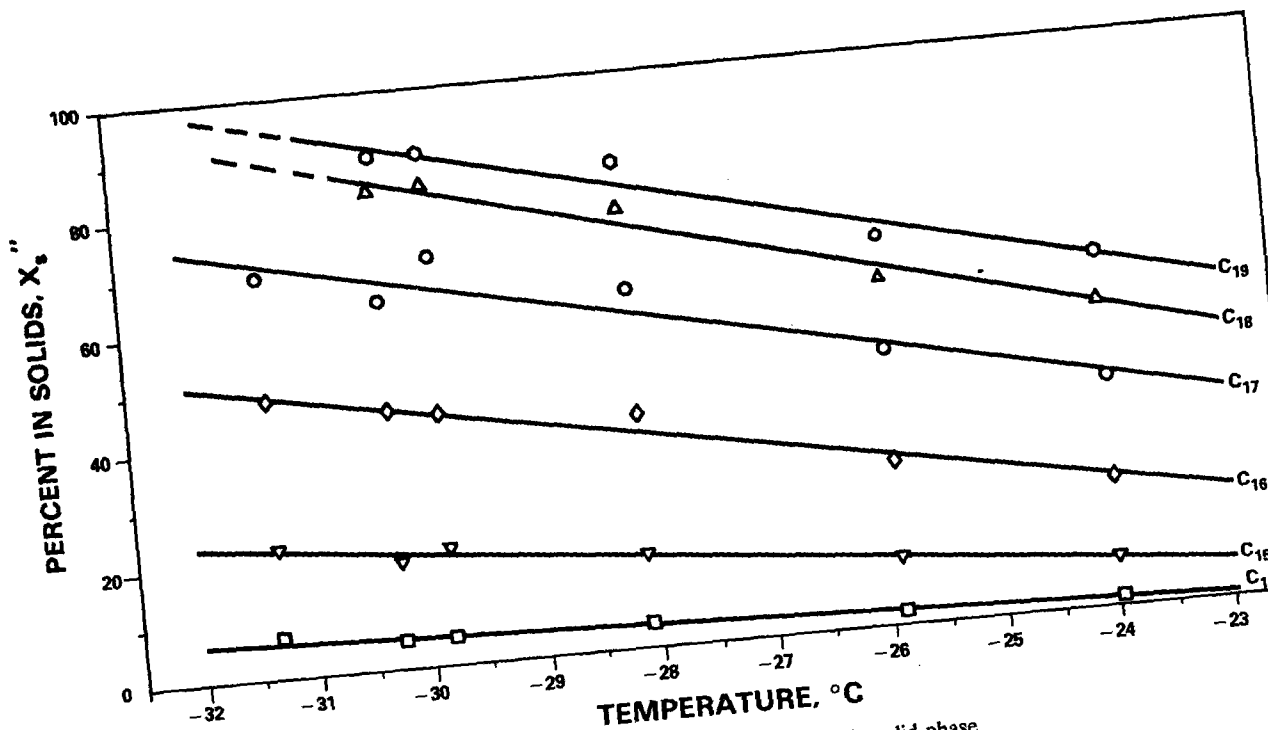


Fig. 13 — Percent of total fuel n-Alkanes found in solid phase.  
Fuel: 82-16, DFM Shale II.

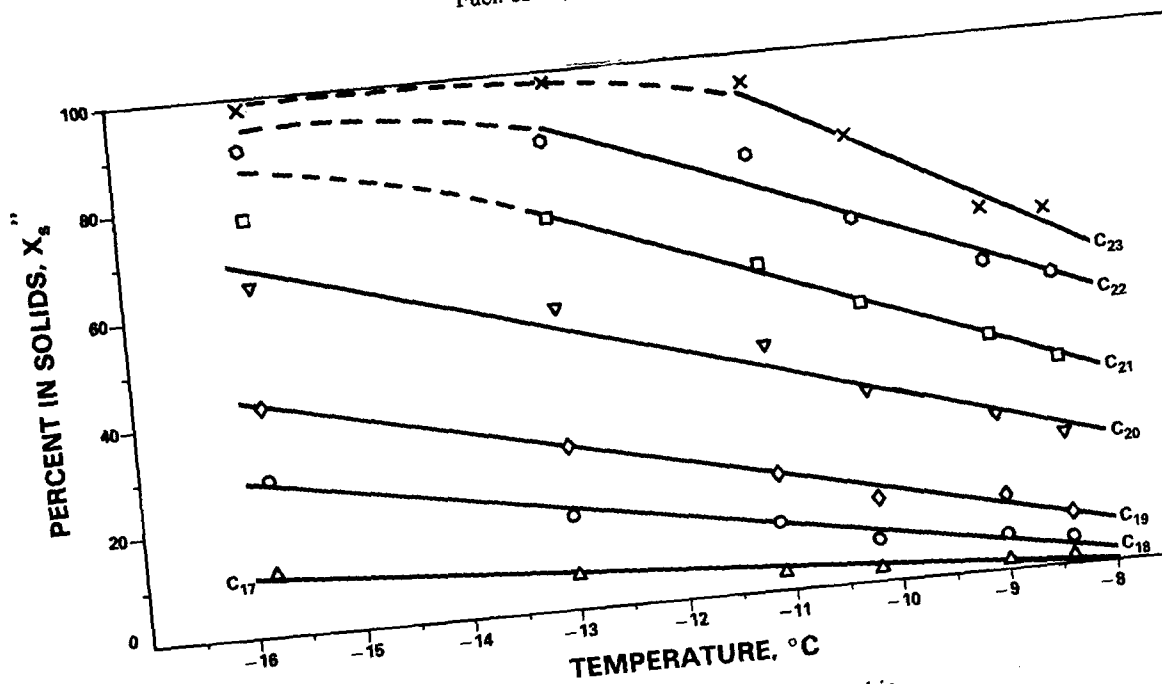


Fig. 14 — Percent of total fuel n-Alkanes found in solid phase. Fuel: 82-8, DFM Petroleum.

For the fuel J-22, the data plotted in Fig. 11 show a slight but steady increase in the percent of  $n\text{-C}_{10}$ , the lowest  $n$ -alkane present that appears in the solid phase, reaching a value of about 4% at  $-58^\circ\text{C}$ . The higher  $n$ -alkanes show increasing amounts appearing in the solid phase with over 75% of  $n\text{-C}_{15}$  in the solids at  $-58^\circ\text{C}$ . It may be, however, that there is no longer a straight-line relationship near this lower temperature for the two highest  $n$ -alkanes, but more data would be required before "leveling off" could be proven. Obviously the percent in the solids must approach 100% more slowly the closer it gets to 100%. If all the lines for the six  $n$ -alkanes are extrapolated to  $X_s'' = 0$  (the freezing point), the freezing point temperature is found to vary from  $-47.2^\circ\text{C}$ , with the average value at  $-47.9^\circ\text{C}$ .

Figure 12 shows the corresponding curves for the fuel 80-5. The data points for  $n\text{-C}_{16}$ , the largest  $n$ -alkane present, are very scattered due to its concentration being so low that it often did not appear on the filtrate chromatogram and its concentration could not be determined. Therefore no plot for  $n\text{-C}_{16}$  appears in Fig. 12. The other  $n$ -alkanes behave in a very similar manner to those in the J-22 fuel. The "leveling off" of the curve for  $n\text{-C}_{15}$  is more apparent in the petroleum-derived JP-5, and this is indicated in Fig. 12. The percent of the  $n$ -alkane in the fuel that is found in the solid phase is lower in all instances in 80-5 than in J-22. This is most probably due both to the lesser amount of solid crystals formed and to the presence of  $n\text{-C}_{16}$  in 80-5, which would be expected to be the first to crystallize out of solution. Because the straight-line plot for  $n\text{-C}_{10}$  reaches a value of only 1.5% at  $-58^\circ\text{C}$ , this curve was not drawn in Fig. 12. When all the curves for the  $n$ -alkanes, including  $n\text{-C}_{10}$  and  $n\text{-C}_{16}$ , are extrapolated to  $X_s'' = 0$ , the freezing point range lies from  $-51.4^\circ$  to  $-45.4^\circ\text{C}$ , with the average value being  $-48.4^\circ\text{C}$ .

The data for fuel 82-16, which follow the same pattern as those for the jet fuels, are plotted in Fig. 13. From Table 17 it is evident that the lighter  $n$ -alkanes,  $n\text{-C}_9$  to  $n\text{-C}_{12}$ , form no solid crystals, and only about 1.2% of  $n\text{-C}_{13}$  present in the fuel is found in the solid phase at  $-32^\circ\text{C}$ . Therefore only the  $n$ -alkanes from  $n\text{-C}_{14}$  through  $n\text{-C}_{19}$  appear in Fig. 13. The concentration of  $n\text{-C}_{20}$  in the filtrate could not be measured in several cases; hence the data points are scattered and are not plotted in Fig. 13. The change with the temperature in the percent of the  $n$ -alkane in the fuel that appears in the solid phase increases with the carbon number for the  $n$ -alkanes  $n\text{-C}_{13}$  to  $n\text{-C}_{18}$ , very much as it did with  $n\text{-C}_{10}$  to  $n\text{-C}_{15}$  in both jet fuels. The percent of  $n\text{-C}_{19}$  found in the solids varies less strongly with the temperature than does that of  $n\text{-C}_{18}$ ; the slope is noticeably less in the graph. This may well be because the percent of  $n\text{-C}_{19}$  found in the solid phase starts "leveling off" before the last two points on the graph are reached. Extrapolation of the  $n$ -alkane curves to  $X_s'' = 0$  gives a range for the freezing point of 82-16 from  $-21.6^\circ$  to  $-10.8^\circ\text{C}$ , with the average value being  $-16.1^\circ\text{C}$ . This may be compared to  $-14.5^\circ\text{C}$ , obtained by extrapolating the curve in Fig. 10 to the point where the total solids,  $S$ , is zero.

There are so many  $n$ -alkanes (seventeen) in the DFM 82-8 fuel that it is to be expected that many of the lower ones would not form crystals in the temperature range investigated. This is clearly true of  $n\text{-C}_8$  through  $n\text{-C}_{14}$ , both from the filtrate data (Table 6) and from the fact that the values of  $Z$  calculated by considering these  $n$ -alkanes as  $k$  compounds do not differ from the values found from the other non- $n$ -alkane components. Data for  $n\text{-C}_{15}$  indicate that some crystals of this compound may be formed, but quantitative accuracy is lacking. Crystals are definitely formed from  $n\text{-C}_{16}$ , and the data form a good straight line. The percent found in the solid phase, however, is only 3.2% at  $-15.8^\circ\text{C}$ , and so for the sake of clarity the curve  $n\text{-C}_{16}$  has been omitted from Fig. 14. For the heavier  $n$ -alkanes shown in Fig. 14, the slopes can be seen to increase with the carbon number except for  $n\text{-C}_{22}$ . Probably the data point at  $T = -13^\circ\text{C}$  should not be included in the least squares fit, since "leveling off" appears to begin at temperatures above this value. The extrapolated temperature at which no crystals are formed ( $X_s'' = 0$ ) varies from  $-7.9^\circ$  to  $-1.2^\circ\text{C}$ , with average being  $-4.6^\circ\text{C}$ . The freezing point extrapolated from Fig. 10 is  $-3.9^\circ\text{C}$ . The agreement between the freezing points determined in these two ways is quite close for all fuels.

The normal alkanes are thus seen to behave as would be expected if they alone freeze or crystallize out of the fuel at temperatures below, but in the vicinity of, the freezing point. The higher the  $n$ -alkane the more completely it is removed from the liquid phase as the temperature decreases.

**n-Alkane Balance**

Perhaps the most important check for self-consistency for the type of data gathered in this study is a material balance for each of the compounds present. For every run, not only was the overall material balance calculated, as reported above, but also a material balance for each of the n-alkanes and *k* compounds. Only samples of the material balances for the n-alkanes are reported here, as they are the components of greater interest. The balances for the *k* compounds turned out to be very similar; the discrepancies, reported as "percent deviation," being in some instances larger probably for the following reason. The n-alkanes present in low concentrations are at the two ends of the chromatogram where there are very few components of the fuel, where the base line is flat, and where the peaks are clear and distinct giving a good degree of accuracy to the quantitative determinations. On the other hand, the *k* compounds were specifically chosen for having their peaks in the main part of the chromatogram. Hence, their peaks are smaller relative to neighboring n-alkane peaks, the base line is not flat in their vicinity, the areas of their peaks are measured "valley to valley" rather than above a straight base line and there are "shoulders" on the peaks in some cases. All of these factors lessen the accuracy with which their concentrations can be determined. In some cases the material balances have deviations from 10 to 20%.

Material balances for all the n-alkanes present are shown in Tables 19 to 22. Each table lists data from one typical run for each of the four fuels. The run can be identified by the temperature for all fuels except J-22, so that the other data for those can be found elsewhere in this report. In the case of J-22 one specific run at the given temperature was chosen for the material; the data given elsewhere in this report represent average values from three separate runs at the given temperature,  $-53.6^{\circ}\text{C}$ .

Seldom are the discrepancies between the "input" (fuel) and "output" (filtrate plus precipitate) greater than 5%, except in cases where the concentrations are extremely low. The method of analysis by the gas chromatography used in this study clearly gave consistently good results.

Table 19 — n-Alkane Balance, Weight in Milligrams. Fuel: JP-22, JP-5  
Shale II. Run No. 30:  $T = -53.6^{\circ}\text{C}$ ,  $Z = 0.767$ .

n-Alkane	Filtrate F	Precipitate P	Liquid in Precipitate, L	Total Liquid F + L	Solids S	Total $F + P \equiv$ $F + L + S$	Fuel	Percent Deviation
C <sub>10</sub>	282	61	55	337	6	343	357	-3.9
C <sub>11</sub>	510	145	100	610	45	655	678	-3.4
C <sub>12</sub>	362	182	71	433	111	544	563	-3.4
C <sub>13</sub>	191	151	38	229	113	342	350	-2.3
C <sub>14</sub>	47	57	9	56	48	104	108	-3.7
C <sub>15</sub>	14	16	3	17	13	30	28	-7.1
TOTAL	1406	612	276	1682	336	2018	2084	-3.2
TOTAL FUEL	6292	1608	1233	7525	375	7900	7934*	-0.4
Percent n-Alkane in Total	22.4	38.1	22.4	22.4	89.6	25.5	26.3	—

\*Starting weight of sample used in Run No. 30

Table 20 — n-Alkane Balance, Weight in Milligrams. Fuel: 80-5, JP-5  
Petroleum. Run No. 48: T = -55.5°C, Z = 0.75.

n-Alkane	Filtrate F	Precipitate P	Liquid in Precipitate, L	Total Liquid F + L	Solids S	Total F + P $\equiv$ F + L + S	Fuel	Percent Deviation
C <sub>10</sub>	74	12	11	85	1	86	83	+3.6
C <sub>11</sub>	282	59	43	325	16	341	360	-5.3
C <sub>12</sub>	303	118	46	349	72	421	442	-4.8
C <sub>13</sub>	173	131	27	200	104	304	312	-2.6
C <sub>14</sub>	56	79	9	65	70	135	138	-2.2
C <sub>15</sub>	15	30	2	17	28	45	45	0
C <sub>16</sub>	4	8	1	5	7	12	12	0
TOTAL	907	437	139	1046	298	1344	1392	-3.4
TOTAL FUEL	6832	1383	1037	7869	346	8215	8260*	-0.5
Percent n-Alkane in Total	13.3	31.6	13.4	13.3	86.1	16.4	16.8	—

\*Starting weight of sample used in Run No. 48

Table 21 — n-Alkane Balance, Weight in Milligrams. Fuel: 82-16, DFM  
Shale II. Run No. 60: T = -28.1°C, Z = 0.72.

n-Alkane	Filtrate F	Precipitate P	Liquid in Precipitate, L	Total Liquid F + L	Solids S	Total F + P $\equiv$ F + L + S	Fuel	Percent Deviation
C <sub>9</sub>	12	2	2	14	0	14	14	0.0
C <sub>10</sub>	38	7	7	45	0	45	43	4.6
C <sub>11</sub>	80	14	14	94	0	94	90	4.4
C <sub>12</sub>	117	21	21	138	0	138	130	6.2
C <sub>13</sub>	181	33	32	213	1	214	206	3.9
C <sub>14</sub>	205	45	36	241	9	250	236	5.9
C <sub>15</sub>	160	64	28	188	36	224	215	4.2
C <sub>16</sub>	102	94	18	120	76	196	186	5.4
C <sub>17</sub>	64	124	10	74	114	188	183	2.7
C <sub>18</sub>	27	102	5	32	98	130	130	0.0
C <sub>19</sub>	8	47	1	9	46	55	55	0.0
TOTAL	994	553	174	1168	380	1548	1488	4.0
TOTAL FUEL	6460	1584	1140	7600	444	8044	8093*	-0.6
Percent n-Alkane in Total	15.4	34.9	15.3	15.4	85.6	19.2	18.4	—

\*Starting weight of sample used in Run No. 60

Table 22 — n-Alkane Balance, Weight in Milligrams. Fuel: 82-8, DFM Petroleum. Run No. 69: T = -10.2°C, Z = 0.83.

n-Alkane	Filtrate F	Precipitate P	Liquid in Precipitate, L	Total Liquid F + L	Solids S	Total F + P $\equiv$ F + L + S	Fuel	Percent Deviation
C <sub>9</sub>	9	1	1	10	0	10	10	0.0
C <sub>10</sub>	29	4	4	33	0	33	33	0.0
C <sub>11</sub>	42	6	6	48	0	48	49	-2.0
C <sub>12</sub>	68	10	10	78	0	78	82	-4.9
C <sub>13</sub>	99	16	16	115	0	115	118	-2.5
C <sub>14</sub>	133	21	21	154	0	154	154	0.0
C <sub>15</sub>	140	22	22	162	0	162	164	-1.2
C <sub>16</sub>	125	21	20	145	1	146	155	-5.8
C <sub>17</sub>	109	21	17	126	4	130	133	-2.3
C <sub>18</sub>	83	21	13	96	8	104	100	+4.0
C <sub>19</sub>	58	23	9	67	14	81	88	-8.0
C <sub>20</sub>	32	26	5	37	21	58	58	0.0
C <sub>21</sub>	18	24	3	21	21	42	41	+2.4
C <sub>22</sub>	8	18	1	9	17	26	25	+4.0
C <sub>23</sub>	0	11	0	0	11	11	13	-15.4
C <sub>24</sub>	0	5	0	0	5	5	6	-16.7
TOTAL	953	250	148	1101	102	1203	1229	-2.1
TOTAL FUEL	6874	1318	1094	7968	224	8192	8251*	-0.7
Percent n-Alkane in Total	13.9	19.0	13.5	13.8	45.5	14.7	14.9	—

\*Starting weight of sample used in Run No. 69

### Determination of Z by Liquid Chromatography

Because the value of Z is of the greatest importance in this study, two other methods for determining it were investigated as a check on the accuracy of the method used, what we call the "k-component method." One of these methods was high-pressure liquid chromatography (LC). Samples of fuel, filtrate, and precipitate for particular runs were analyzed for three classes of compounds: saturated, monocyclic, and dicyclic aromatic hydrocarbons. The fuel sample contained no internal standard, but in one case (with J-22) the filtrate and precipitate each had an internal standard, iso-octane, added to it. Since iso-octane is a saturated hydrocarbon and was present to about 9% by weight, the percentages of the three fractions determined by LC had to be adjusted for no iso-octane present.

Table 23 gives the results of the LC analyses, one for Run No. 30 at -53.6°C with J-22 fuel, Shale-II-derived JP-5, and the other for Run No. 76 at -56.3°C using fuel 80-5, petroleum-derived JP-5. For the former, both the percentages obtained by LC analysis of the precipitate and filtrate containing iso-octane and the adjusted values are listed. As expected, the percent of saturated hydrocarbons is greater in the precipitate than in the filtrate, whereas the reverse is true for the monocyclic and dicyclic aromatic hydrocarbons. To calculate Z, we first assume that no dicyclic aromatic hydrocarbons freeze or crystallize out of the fuel. Then this fraction can be assumed to be a k compound. By Eq. (12),  $Z = 0.78/1.02 = 0.765$ , total solids S = 4.8%, and saturated hydrocarbons making up 97.5% of S. By GC analysis, using components a and b as k compounds, Z for Run No. 30 was determined to be 0.766 and S = 4.8%, with the normal alkanes comprising 89.6% of the solids. The agreement between the two methods seems almost too close.

Table 23 — Hydrocarbon Fractions Determined by High-Pressure Liquid Chromatography

a) Fuel: J-22, JP-5 Shale II. Run No. 30: T = -53.6°C					
Hydrocarbon Fraction	Percent in Fuel	Percent in Filtrate* Precipitate*		Percent in Filtrate** Precipitate**	
Saturated	76.58	75.01	80.23	75.52	80.70
Monocyclic aromatics	22.45	23.99	19.00	23.46	18.51
Dicyclic aromatics	0.97	1.00	0.77	1.02	0.78
b) Fuel: 80-5, JP-5 Petroleum. Run No. 76: T = -56.3°C					
Hydrocarbon Fraction	Percent in Fuel	Percent in Filtrate Precipitate			
Saturated	76.99	76.40	79.88		
Monocyclic aromatics	18.08	18.21	15.86		
Dicyclic aromatics	4.93	5.39	4.26		

\*iso-octane present as internal standard

\*\*Adjusted for no iso-octane

If the assumption is made that neither monocyclic nor dicyclic aromatic compounds appear in the solid phase, the value of  $Z$  becomes 0.78, the average value taking both the monocyclic and dicyclic aromatic components as  $k$  compounds. The total solids  $S$  becomes 4.5%, still in remarkably close agreement to the GC analysis.

The results of the analysis by LC of the run made with the fuel 80-5, petroleum-derived JP-5, at -56.3°C are also given in Table 23. Since none of the samples analyzed contained an internal standard, the value of  $Z$  could be determined directly from the data. Considering the dicyclic aromatic hydrocarbons as  $k$  compounds,  $Z$  is found to be  $4.26/5.39 = 0.79$ , and the total solids  $S = 5.5$ , with saturated hydrocarbons accounting for 91.9% of the solids. This compares favorably with the GC analysis, according to which  $Z = 0.80$  and  $S = 5.3\%$ , although the normal alkanes comprised only 76.5% of the solids (see Table 12). If, however, both the monocyclic and dicyclic aromatic compounds are considered as  $k$  components, the average value of  $Z = 0.83$ , with  $S = 4.5\%$ . The value of  $Z = 0.87$  obtained by considering monocyclic hydrocarbons as  $k$  components is extremely high and gave results not compatible with the GC results.

In general, however, it may be concluded that high pressure LC corroborated the results we obtained by GC.



### Determination of Z by Dye Tracers

A recent paper by Moynihan et al. [16] reports values of the amounts of crystalline solids, S, formed in partially frozen samples of fuel J-22 over the same temperature range in which we were studying the same fuel. In order to determine the amounts of crystalline solids, they used an apparatus similar to our LSS to separate the filtrate and precipitate fractions, but they used hydrocarbon-soluble liquid dyes as tracers, similar in function to our *k* compounds, followed by spectrophotometric analysis in place of our GC analysis. Because of the difficulty we were experiencing with the other fuels in obtaining truly consistent and reproducible values of Z, we decided to try the dye method together with the GC and *k* compound method.

First, however, we made a comparison of the results we had obtained using the GC method on the J-22 fuel with calculated results based on the data reported by Moynihan et al. [16]. Values they had obtained for the total solids S can be read directly for the temperatures at which we had made our investigations with J-22 fuel. From this the value of Z can be calculated directly by using our data for the filtrate and precipitate fractions. Then the concentrations of all the n-alkanes in the solids can be determined. If these concentrations are calculated in weight percent, then the total n-alkane concentrations should be close to, but never greater than, 100%.

Table 24(a) lists the results of the GC-*k*-compound method for determining Z, S, and percent total n-alkanes in the solids, and also the results for these calculated by the dye method using data from Ref. 16. The highest temperature we investigated,  $-48.5^{\circ}\text{C}$ , was above the reported melting point of  $-49.8^{\circ}\text{C}$  as determined by the "static method," i.e., the disappearance of crystals [16]; hence, no comparison is possible at that temperature. At  $-57.5^{\circ}\text{C}$ , the lowest temperature we investigated, the results are reasonably close; a change of 0.01 or 0.02 in either value of Z could bring the figures into very close agreement. The value of 101% for the total n-alkane concentration in the solids is not unacceptable; a change of 0.01 in the value of Z could change this value by 5%.

When the values of S corresponding to the three higher temperatures which we investigated were taken from the graph in Ref. 16, the values of Z calculated thereby for our data were much greater than the values of Z obtained by the *k*-compound method with GC analysis. Furthermore the percentage of total alkanes in the solids by the dye technique was calculated to be very much greater than 100% in all three cases, which is simply impossible. It was therefore concluded that the *k*-compound method with GC analysis gave more consistent results than those calculated from data using the dye method.

Before the calculations mentioned above had been made using the dye method data in Ref. 16, we carried out nearly all the experiments on fuel 82-16, most of those on fuel 80-5, and a few on fuel 82-8 using both the dye method with spectrophotometric analyses and the *k*-compound method with GC analysis. The results of the two methods are listed for comparison in Table 24(b,c,d).

The dyes used were the same ones used by Moynihan et al. [16], two hydrocarbon-soluble liquid dyes, obtained from American Cyanimid Co., Boundbrook, NJ, and identified as CALCO Oil Orange R Liquid and CALCO Oil Blue G Liquid. The properties of these dyes and the method of analysis are reported by Moynihan et al. [16]. Suffice it to say that we used the 480-nm peak of the blue dye and the 652-nm and 603-nm peaks of the orange dye. The spectrophotometer used to carry out the analyses was a Cary 14.

There were difficulties—previously mentioned—separating the filtrate and precipitate fractions and obtaining "good" values of Z. By "good" we mean values close to 100% for the total percentage of n-alkanes in the solids, S. We decided to use the dyes as "tracers" whereby we could obtain, independently, values of Z to compare with the ones obtained by the *k*-compound method. The criteria on which to judge between the two methods would be (1) the relationship between the percent crystalline

Table 24 — Comparison of Values of Z, Percent Solids S, and Percent Total n-Alkanes in Solids Determined by *k*-Compound and Dye Methods

a) Fuel: J-22, JP-5 Shale-II*										
°C	-57.5		-55.3		-53.6		-51.4			
Method	<i>k</i>	Dye	<i>k</i>	Dye	<i>k</i>	Dye	<i>k</i>	Dye	<i>k</i>	Dye
Z	0.85	0.88	0.76	0.86	0.77	0.88	0.67		0.99	
Solids, S	8.2	6.7	7.3	4.3	4.5	2.5	2.9		0.11	
n-Alkanes in S	95.7	101.0	80.9	122.0	95.6	156.0	83.1		> 1000	

b) Fuel: 80-5, JP-5 Petroleum										
°C	-57.5		-55.1		-53.6		-53.5		-51.4	
Method	<i>k</i>	Dye	<i>k</i>	Dye	<i>k</i>	Dye	<i>k</i>	Dye	<i>k</i>	Dye
Z	0.70	0.74	0.69	0.79	0.83	0.92	0.78	0.84	0.77	0.76
Solids, S	6.1	5.2	5.7	3.8	4.0	1.9	3.2	2.3	2.9	2.8
n-Alkanes in S	76.0	86.2	59.8	82.2	65.9	128.0	80.3	106.0	58.9	55.7

c) Fuel: 82-16, DFM Shale-II										
°C	-30.5		-29.8		-28.1		-25.9		-24.0	
Method	<i>k</i>	Dye	<i>k</i>	Dye	<i>k</i>	Dye	<i>k</i>	Dye	<i>k</i>	Dye
Z	0.72	0.65	0.77	0.69	0.72	0.67	0.78	0.72	0.72	0.68
Solids, S	5.9	7.4	5.8	7.8	5.5	6.5	4.6	5.9	3.6	4.2
n-Alkanes in S	82.8	67.9	92.3	62.5	85.4	73.4	76.2	61.3	83.9	74.6

d) Fuel: 82-8, DFM Petroleum**				
°C	-11.1		-10.2	
Method	<i>k</i>	Dye	<i>k</i>	Dye
Z	0.78	0.85	0.83	0.82
Solids, S	2.6	1.7	2.7	2.9
n-Alkanes in S	60.7	87.6	45.3	43.1

\*Z derived from S, which was taken from Ref. [16]

\*\*Dyes used on only two runs with this fuel

solids  $S$  and the temperature  $T$ , and (2) the total percentage of all the  $n$ -alkanes in the solid phase should not exceed 100%.

For the fuel 80-5, five of the nine runs were made with dyes and four without. The values of  $Z$ ,  $S$ , and total  $n$ -alkanes percentage in the solids calculated by both the  $k$ -compound method and dye method are listed in Table 24 (b). Considering criterion (2) above, it is clear that the dye method gave results closer to 100%-total alkanes in two cases, at temperatures of  $-57.5^\circ$  and  $-55.1^\circ\text{C}$ . The dye method gave unacceptable values at temperatures of  $-53.6^\circ$  and  $-53.5^\circ\text{C}$ , where the total alkane percentage greatly exceeded 100%. In the fifth case,  $T = -51.4^\circ\text{C}$ , the results were in good agreement. Considering criterion (1), the data using the dye method were far more scattered than were the data determined by the  $k$ -compound method (Fig. 10).

In five of the six experimental runs using the fuel 82-16, the dye method was used as well as the  $k$ -compound method. The results for comparison appear in Table 24(c). For both the JP-5 fuels, the dye method gave  $Z$  values higher than did the  $k$ -compound method. This was not so for the shale-derived DFM. In every case the value of  $Z$  was lower, as was the percentage of total  $n$ -alkanes in the solid phase. Furthermore the data relating the percent solids  $S$  to the temperature were widely scattered; a good straight line could not be drawn through them.

For the fourth fuel, 82-8, only two of the runs were made with the dyes, and the results are listed in Table 24(d). It can be seen that the dye method gave results closer to 100% in one case; in the other the two methods gave very similar results. Since the use of dyes as "tracers" had not proven as good a method as the GC analysis based on  $k$ -compounds, the dye method was abandoned for the remaining experiments.

### Composition of the Solid Phase

Probably the most important and certainly the most difficult task we had was the determination of the composition of the solid phase. Tables 7 to 10 give the normalized concentrations of each  $n$ -alkane in the solids. The actual concentrations can be readily calculated by multiplying the value in the tables by the concentrations of each  $n$ -alkane in the fuels, which are listed in Table 2. Table 24 lists the sum of the  $n$ -alkane concentrations in the solids, or the total  $n$ -alkane concentration, for a great many of the experiments.

In the case of the J-22 fuel, at two temperatures,  $-57.5^\circ$  and  $-53.6^\circ\text{C}$ , the  $n$ -alkanes account for over 95% of the solids formed. If the value of  $Z$  at  $-51.4^\circ\text{C}$  were 0.71 rather than 0.67, the  $n$ -alkanes would then total more than 95% of the solids. In the same way an increase in  $Z$  at  $-55.3^\circ\text{C}$  from 0.76 to 0.80 would bring the percentage of  $n$ -alkanes in the solids to over 90%. Thus an accurate determination of  $Z$  is of the greatest importance. It would seem that the normal alkanes comprise at least 95%, and perhaps more, of the solids formed by partially freezing J-22 fuel at the temperatures investigated. About 1% seems to be due to the components  $c$ ,  $d$ , and  $e$ . While the concentration of these is less in the precipitate than in the filtrate, it is not so much less that a small amount could not crystallize out. Thus there are undoubtedly some other compounds in the 67% of the J-22 fuel that are not made up of  $n$ -alkanes or of the components  $a$ ,  $b$ ,  $c$ ,  $d$ , and  $e$  that form some crystals in the solids. But no components other than the  $n$ -alkanes could be found having higher concentrations in the precipitate than in the filtrate. Hence components other than the  $n$ -alkanes did not form crystals to any great extent.

The same is true for the fuel 80-5, the petroleum-derived JP-5, even though the percentage of  $n$ -alkanes is only two-thirds that in J-22, and the GC trace shows it to be of considerably more complex composition. The difficulty here arises in that in no case did the calculated total percentage of  $n$ -alkanes in the solid exceed 80% (cf. Table 24). Something has to account for some 20% of the solids.

It may be that the values of  $Z$  are not very accurate for this fuel and that another method should be found by which to obtain accurate values.

For the shale-derived DFM, fuel 82-16, better and more consistent values for the percentage of n-alkanes in the solids were obtained. The fuel derived from shale is less complex in composition than a petroleum-derived fuel, and better results seem to be obtained from these fuels. The average value for the percent total n-alkanes in the solids, listed in Table 24, is 84%, again somewhat lower than the 100% predicted if the solid is comprised only of n-alkanes.

The results from the experiments carried out with the petroleum-derived DFM, fuel 82-8, are poorer than those from its shale-derived counterpart. The average of the calculated n-alkane percentage in the solids is only 53.6%, considerably less than expected. This is an average of all six runs (only two runs are listed in Table 24(d)). Since only 15% of the fuel consists of n-alkanes, and since the chromatogram is extremely complex, it may well be that there are a great many components that contribute very small amounts of crystals, but it seems hard to conceive that 40% of the composition of the solids can be accounted for in this way. Certainly until other methods of analysis can be devised to measure accurately these small amounts of many different components, or until the solid crystals can in some way be separated completely from the entrapped liquid and then analyzed, the complete composition of the solid crystalline phase will remain undetermined. Some useful information might be gathered, however, by partially freezing some mixtures of normal alkanes and one or two other components and determining their distribution coefficients. From this, extrapolation to their behavior in fuels might be made and tested.

## 5. SUMMARY AND CONCLUSIONS

The liquid (filtrate) and the solid crystals containing a large portion of entrapped liquid (precipitate) from partially frozen samples of four middle distillate fuels were separated from each other and collected by means of the NRL liquid-solid separator (LSS). This was done at several temperatures, each below the freezing point of the original fuel samples. The collected precipitates and filtrates were analyzed quantitatively for the normal alkanes and other specifically designated components ( $k$ -compounds) by gas chromatography as were the original fuel samples. The filtrate data were straightforward, and Van't Hoff plots of the n-alkane concentrations (log concentration vs reciprocal absolute temperature) formed straight lines and their slopes demonstrated the importance of the higher n-alkanes in fuel freezing, or crystallization, at cold temperatures.

The precipitate data presented some problems of interpretation since it was observed that the waxy crystal matrix entrapped significant amounts of liquid (filtrate). Modifications were made in the LSS apparatus to remove this entrapped liquid. More of the liquid was removed in this way, but it was evident that there still remained considerable liquid in the clathrate-type crystalline matrix formed by the solid material. An indirect method (using the  $k$ -compound) was derived to estimate the n-alkane concentrations in the solid fraction of the precipitate. Two other methods were investigated to improve on this method: one using dyes as a "tracer" proved less satisfactory; the other using high-pressure liquid chromatography, a tedious method, validated the method used.

The solid data, thus estimated, demonstrated that the higher n-alkanes play the key role in fuel crystallization at low temperatures, concentrating as much as tenfold in the crystallized solids compared to the liquid. Also it was clearly shown that the n-alkanes form the major part, up to at least 95% by weight in some fuels, of the solid crystals formed.

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## 8. NOMENCLATURE

	<u>Fuel Sample</u>	<u>Filtrate</u>	<u>Precipitate</u>	<u>Precipitate Fraction</u>	
				<u>Solids</u>	<u>Liquid</u>
<u>Total Material:</u>					
Weight	$W_o$	$W_F$	$W_P$	$W_S$	$W_L$
Fraction of Sample		$F = W_F/W_o$	$P = W_P/W_o$	$S = W_S/W_o$	$L = W_L/W_o$
<u>SPECIES a or k:</u>					
Weight	$w_o$	$w_F$	$w_P$	$w_S$	$w_L$
Concentration (w/W)	$X_o = w_o/W_o$	$X_F = w_F/W_F$	$X_P = w_P/W_P$	$X_s = w_S/W_S$	$X_L = w_L/W_L$
$Z = W_L/W_P$					
a = Crystalline Species					
k = Noncrystalline Species					
<u>Subscripts:</u>			<u>Superscripts:</u>		
o = Original Sample			' = Normalized Data (Concentration di- vided by that of original sample)		
F = Filtrate					
P = Precipitate			" = Percent concentration of a species in the fuel found in the solid phase		
S = Solids Fraction of Precipitate (Crystals)					
L = Liquid Fraction of Precipitate					
T = Total					